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ELECTRON CORRELATION IN METALS

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SHEFFIELD, ENGLAND

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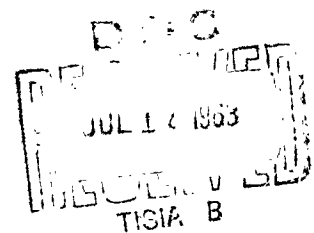
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FOREWORD

This final technical report covering the period 1 November 1959 -
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Abstract

     The first and second-order density matrices for a uniform electron gas are discussed in the limiting cases of weak coupling (usual gas parameter $r_s \to 0$) and strong coupling ($r_s \to \infty$). Attention is focussed on the important pair distribution function and on the momentum distribution. If the high density form of the momentum distribution as given by Daniel and Vosko (1960) is adopted, then conclusions can be drawn regarding the meaning of a Fermi surface in a system of interacting particles.

     However, the applicability of perturbation theory to the calculation of the momentum distribution is thrown into some doubt by a calculation we have carried out on a soluble problem. Here we find that the perturbative answer is not correct, but unfortunately the problem, that of non-interacting electrons in a magnetic field, is very different physically from the Coulomb correlation case. Further work therefore remains to be done on this point.

     Variational forms of second-order density matrices are discussed, and the Euler equations are obtained for one possible scheme based on localized orbitals.

     Finally, some progress on the non-uniform gas is briefly reported.

CONTENTS

List of Publications

1. Electron correlation in metals: density matrix approach, by N. H. March and S. Sampanthar, Acta Physica Hungarica, 14, 61, 1962 (invited paper read at Balatonfoldvar Theoretical Physics Conference, 1961).

2. The energy and the Dirac density matrix of a non-uniform electron gas, by W. Jones, N. H. March and S. Sampanthar, Physics Letters, 1, 303, 1962.

List of Illustrations

Figure 1

Pair functions for an electron gas.

Figure 2

Momentum distribution in an electron gas.

1. Introduction

The problem of dealing with the Coulomb interactions between conduction electrons in metals has proved very formidable and no complete solution has, as yet, been found. In recent years, beginning with the important investigation of Macke (1950), attention has been focussed primarily on the use of perturbation theory. Unfortunately, the perturbation expansion does not prove useful in practice in the range of real metallic densities, which are characterized by the usual gas parameter r_s lying in the range $2 < r_s < 5 \cdot 5$.

In this report, we consider chiefly methods based on a variational approach to the correlation problem, although considerable use is made of results obtained in the limiting cases of weak $(r_s \to 0)$ and strong $(r_s \to \infty)$ coupling.

Certain very important questions connected with the meaning of a Fermi surface in a system of strongly interacting particles are not finally answered, but some light is thrown on the general problem in sections 2 and 3 of the Report.

While most of the work has been concerned with the uniform electron gas, some progress on the non-uniform problem is described in section 6. Here, a good deal of work remains to be carried out.

We should mention that our earlier work on spin density waves has not been included in this Report, because, after our

variational calculations were completed more powerful methods
were developed by Overhauser and our own work is therefore, at
most, of historical interest.

2. Coulomb correlations in a uniform electron gas

We discuss first the role of electron interactions in a uniform system. Throughout, we shall focus attention on density matrices, and in sections 2.2 and 2.3 we present results in the Sommerfeld model which are valid for the limiting cases of low and high density respectively. Some inferences concerning the Fermi surface are drawn in section 2.4, but no completely final result on the change in the momentum distribution as the interaction strength is varied can be obtained, as some doubts exist as to the validity of perturbation theory in calculating this quantity. Some examination of this point is carried out in section 3 therefore.

2.1 The Hamiltonian and definitions of density matrices for uniform electron gas

We require basically to calculate the ground-state wave function $\psi(x_1 x_2 \ldots x_N)$ for a system of N electrons, where x_i denotes the space co-ordinates r_i and spin co-ordinates σ_i, from the Schrödinger equation

$$H\psi = \varepsilon\psi. \qquad (2.1.1)$$

We adopt as the Hamiltonian of the Sommerfeld model:

$$H = -\tfrac{1}{2} \sum_{1}^{N} \nabla^2_{r_i} + \sum_{i<j} \frac{1}{|r_i - r_j|} - \frac{3}{4\pi r_s^3} \sum_{1}^{N} \int \frac{dr_0}{|r_i - r_0|} +$$

$$+ \tfrac{1}{2} \left(\frac{3}{4\pi r_s^3}\right)^2 \iint \frac{dr_0 \, dr_1}{|r_0 - r_1|} , \qquad (2.1.2)$$

where the last two terms in (2.1.2) refer to the electron-positive background interaction and the background self-energy, respectively. We now define first and second-order spinless density matrices $\gamma(r_1{}'\ r_1)$ and $\Gamma(r_1{}'\ r_2{}'\ r_1\ r_2)$ by the equations

$$\gamma(r_1{}'r_1) = N \int \psi^*(r_1{}'\sigma_1 x_2 \ldots x_N)\psi(r_1\sigma_1 x_2 \ldots x_N)d\sigma_1 dx_2 \ldots dx_N, \qquad (2.1.3)$$

$$\Gamma(r_1{}'r_2{}'r_1 r_2) = \frac{N(N-1)}{2} \int \psi^*(r_1{}'\sigma_1 r_2{}'\sigma_2 x_3 \ldots x_N)\psi(r_1\sigma_1 r_2\sigma_2 x_3 \ldots x_N)$$

$$d\sigma_1 \, d\sigma_2 \, dx_3 \ldots dx_N. \qquad (2.1.4)$$

We note now that the diagonal elements of γ and Γ have direct physical interpretations. Thus $\gamma(r_1\ r_1)$ gives the particle density, which in the Sommerfeld model is simply the constant

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$3/4\pi r_s{}^3$, while $\Gamma(r_1 r_2 r_1 r_2)$ is effectively the probability of electron separation or the pair distribution function. Then, as Mayer (1955) was the first to show, the energy per particle ϵ/N is given by

$$\frac{\epsilon}{N} = -\left(\frac{3}{2\pi r_s{}^3}\right)^{-1} \left[\nabla^2{}_r \gamma(r',r)\right]_{r'=r} - \frac{3}{2r_s{}^3} \int_0^\infty (1 - F(\zeta))\zeta d\zeta, \quad (2.1.5)$$

where $F(\zeta) = F(|r'-r|)$ is the pair function, normalized to unity for large $|r'-r|$.

Since we shall utilize the results later, we note that the usual Hartree-Fock solution based on a determinant of plane waves yields the forms:

$$\gamma(r'r) = \frac{k_f{}^3}{\pi^2} \frac{j_1(k_f|r'-r|)}{k_f|r'-r|} : j_1(\rho) = (\sin \rho - \rho \cos \rho)/\rho^2 \quad (2.1.6a)$$

$$F(r'r) = 1 - \frac{9}{2} \left\{ \frac{j_1(k_f|r'-r|)}{k_f|r'-r|} \right\}^2,$$

where k_f is the magnitude of the wave vector at the Fermi surface and is related to the mean interparticle spacing by

$$k_f r_s = \left(\frac{9\pi}{4}\right)^{\frac{1}{3}} . \quad (2.1.7)$$

Using atomic units, it follows from (2.1.5) and (2.1.6) that the energy per particle is

$$\frac{\epsilon}{N} = \frac{3}{10} \left(\frac{9\pi}{4}\right)^{\frac{2}{3}} \frac{1}{r_s{}^2} - \frac{3}{4\pi} \left(\frac{9\pi}{4}\right)^{\frac{1}{3}} \frac{1}{r_s} . \quad (2.1.8)$$

2.2 Pair function and first-order matrix in low-density limit

The low-density form of the pair function has been discussed earlier by March and Young (1959) using the electron lattice model of Wigner (1938). We simply summarize the results by saying that as r_s becomes very large, the electrons relative to a given particle we have singled out, and placed at the origin of co-ordinates sit on the sites of a body-centred cubic lattice. As r_s is then reduced somewhat, the electrons can be thought of as represented by harmonic oscillator functions

$$\psi = \left(\frac{\alpha}{\pi}\right)^{\frac{3}{4}} \exp\left(-\frac{\alpha r^2}{2}\right) ; \quad \alpha = r_s^{-\frac{3}{2}} . \tag{2.2.1}$$

The results obtained by March and Young (1959) for the pair function are represented in curves 1 and 2 of Fig. 1, for cases $r_s = 100$ and $r_s = 4$. For comparison, the Fermi hole result given in (2.1.6) is also shown in curve 3. We emphasize that while curve 1 should be reliable, curve 2 represents an extrapolation beyond the range of validity of the low density form (2.2.1), and is given solely to show the qualitative influence of varying r_s.

We shall now indicate how this work may be generalized to yield the first-order density matrix and momentum distribution for a low-density gas. From the orbitals (2.2.1), centred on each lattice site, we build a Dirac density matrix. This will not of course, contain the condition of translational invariance,
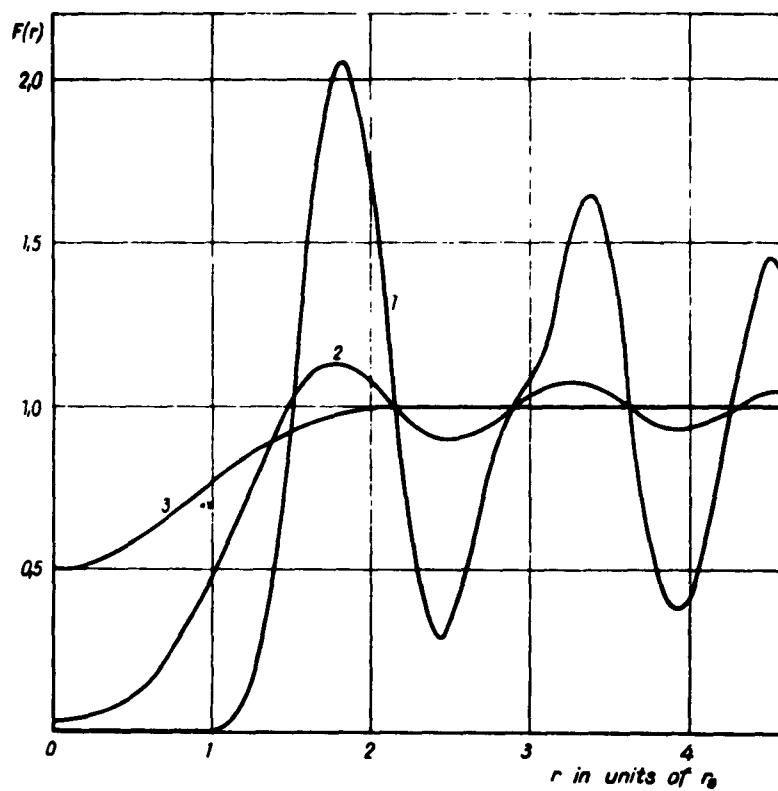
Fig. 1. Pair functions for an electron gas

Curve 1. Low density form for r_s 100
Curve 2. Extrapolated low density form for $r_s = 4$
Curve 3. Hartree-Fock pair function of eqn. (2.6). correct in limit $r_s \to 0$

that is the diagonal element will not be a constant. To obtain a result consistent with the Sommerfeld model we must average over all positions, and then the desired first-order density matrix is easily shown to be

$$\gamma(r'r) = \frac{k_f^3}{3\pi^2} \exp\left(-\frac{\alpha}{4} |r'-r|^2\right). \qquad (2.2.2)$$

The form (2.2.2) as is easily seen, satisfies all the essential conditions, but its range of validity is, of course, restricted, as we shall discuss below. Nevertheless, in conjunction with the high density results of §2.3, it may be used to draw some interesting conclusions about the Fermi surface (see §2.4).

At this stage, it is enlightening to examine the momentum distribution corresponding to the first-order matrix (2.2.2), and this may be found as follows. We require the occupation numbers $P(k)$ of plane wave states $V^{-\frac{1}{2}}e^{-ik \cdot r}$, where V is the volume of the metal and thus we write

$$\gamma(r'r) = \frac{2}{V} \sum_k P(k)e^{-ik \cdot r'} e^{ik \cdot r}, \qquad (2.2.3)$$

or remembering that the density of states in k is $(1/8\pi^3)$ V and using Bauer's expansion for a plane wave as a series of spherical waves:

$$\gamma(r'r) = \frac{1}{4\pi^3} \int_0^\infty P(k) \frac{\sin k|r'-r|}{k|r'-r|} 4\pi k^2 dk. \qquad (2.2.4)$$

It is convenient at this point to measure k in units of the Fermi

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momentum k_f, that is we write $K = k/k_f$, and then (2.2.4) becomes

$$\gamma(r'r) = \frac{k_f^3}{\pi^2} \int_0^\infty P(K) \; \frac{\sin k_f K|r'-r|}{k_f K|r'-r|} \; K^2 \, dK. \quad (2.2.5)$$

Inverting this relation and using (2.2.2) for $\gamma(r'r)$ we find

$$P(K) = \frac{3\pi^{\frac{1}{2}}}{r_s^{\frac{3}{2}}} \exp\left\{ - \left(\frac{9\pi}{4}\right)^{\frac{2}{3}} r_s^{-\frac{1}{2}} K^2 \right\} \quad (2.2.6)$$

where we have eliminated k_f using (2.1.7). As we have remarked earlier, the range of validity of (2.2.6) is restricted, because the orbitals ψ on different lattice sites have been assumed orthogonal, whereas this is only rigorously true in the limit $r_s \to \infty$. However, a rough estimate of the range of validity may be obtained by noting that the occupation numbers $P(K)$ must always lie between 0 and 1. Since $P(K)$ as given by (2.2.6) has its maximum at $K = 0$, we must have that

$$\frac{3\pi^{\frac{1}{2}}}{r_s^{\frac{3}{2}}} < 1 \quad (2.2.7)$$

or

$$r_s > 9\cdot3.$$

The kinetic energy per particle, in the approximation implied by (2.2.6), is easily shown to be

$$\frac{T}{N} = \frac{3}{4r_s^{\frac{3}{2}}}, \quad (2.2.8)$$

in agreement with Wigner (1938). Later treatments based on more

careful study of the dynamics of the vibrating electron lattice
(Coldwell-Horsfall and Maradudin, 1960; Carr, 1961) change (2.2.8)
somewhat, but will not affect the overall validity of the
argument presented above. We note finally for the low-density
limit, that the momentum distribution is a classical 'Maxwell-
Boltzmann' form: this is in sharp contrast to the high density
results to which we now turn.

2.3 Pair function and first-order density matrix in high-density limit

Using the perturbation theory of Gell-Mann and Brueckner
(1957) in suitable form, we shall now discuss the way in which
the pair function and the first-order density matrix develop
from the Hartree-Fock forms given in §2.1 equation (2.1.6). In
order to do so, it is very convenient to introduce a generalization
of density matrices to include also the time: this will greatly
facilitate the setting up of useful equations from which the
matrices can be determined. As a simple example, let us
consider the Dirac first order density matrix for a system
described by a single Slater determinant formed from one-body
orbitals $\psi_1(r)$. This may be written

$$\gamma(r'r) = \sum_1 \psi_1^*(r')\psi_1(r), \qquad (2.3.1)$$

where the summation is over the occupied energy states. However,

if we now introduce a generalized first-order density matrix

$$\gamma(r't'rt) = \sum_i \psi_i^{\,*}(r')\psi_i(r)e^{-iE_it'}\,e^{iE_it},\qquad (2.3.2)$$

where E_i are the occupied energy levels, then this is easily shown to satisfy the equation

$$H\gamma = i\,\frac{\partial\gamma}{\partial t}\,,\qquad t \neq t' \qquad (2.3.3)$$

and this may be used to calculate γ. But in fact, the above time-dependent matrix, is a special case of the one-particle Green's function used by the field theorists in their approach to the many-body problem (see, for example, Klein and Prange, (1958)).

Indeed, the convenient way to make the connection is now to start out from the definition of the Green's functions and the equations which they satisfy. The Green's functions or propagators are suitably defined matrix elements of Heisenberg field operators taken between exact eigenstates of the system. Following Klein and Prange we may write the one-particle and two-particle Green's functions as

$$G(xx') = i < N\; T\{\psi(x)\;\psi^*(x')\}\; N > \qquad (2.3.4)$$

and

$$G(x_1x_2x_3x_4) = i^2 < N\; T\{\;\psi(x_1)\psi(x_2)\psi^*(x_4)\psi^*(x_3)\}\; N >, \qquad (2.3.5)$$

where T is the time ordering operator of Wick. Then if we denote

the particle interaction by $v(r_{12})$ we have the following equation for $G(x, x')$

$$\left(\frac{1}{2} \nabla^2 + i \frac{\partial}{\partial t}\right) G(x,x') = i \int d^3r'' v(r-r'') G(r''trt, r''t'r't') - \delta^4(x-x')$$
(2.3.6)

and this reduces to $(2.3.3)$ when the interaction is neglected. Also we have

$$G(x_1 x_2 x_3 x_4) = G(x_1 x_3) G(x_2 x_4) - G(x_1 x_4) G(x_2 x_3) +$$

$$+ \int d^4y_1 \ d^4y_2 \ d^4z_1 \ d^4z_2 \ G(x_1 y_1) G(x_2 y_2) I(y_1 y_2 z_1 z_2) G(z_1 z_2 x_3 x_4).$$
(2.3.7)

Here I is a complicated interaction operator, which depends on the Green's functions and therefore to obtain exact solutions seems out of the question. However, as we discuss below, in the high density limit it appears possible to make progress in the electron gas problem by inserting the first approximation for $G(x_1 x_2 x_3 x_4)$ inside the integral, provided we approximate sufficiently carefully to the interaction operator. By now writing down the expectation value of the Hamiltonian, we make the indentification between the Green's functions defined here and the density matrices of §2.1, and the results may be stated as follows:

$$\underset{t'\to t+}{\text{Lt}} \ G(r \ t \ r' \ t') = - i\gamma(r' \ r) \qquad (2.3.8)$$

and

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$$\underset{t'\to t+}{Lt}\ G(r\ t\ r'\ t\ r_1'\ t'\ r_2'\ t') = -\ 2\Gamma(r_1'\ r_2'\ r\ r'). \qquad (2.3.9)$$

Proceeding to the high-density gas problem we make use of the work of Kanazawa and Watabe (1960), which shows that in the high density limit we must approximate I by

$$I(y_1 y_2 z_1 z_2) = \delta^4(y_1 - z_1)\ \delta^4(y_2 - z_2)\ iV(y_1 - y_2), \qquad (2.3.10)$$

where the modified interaction V is given by

$$V(y_1 - y_2) = v(y_1 - y_2) + \int d^4x\ d^4y\ v(y_1 - x)\ G_0(x - y)$$

$$G_0(y - x)\ V(y - y_2). \qquad (2.3.11)$$

Here G_0 is the first-order Green's function in the Hartree-Fock limit and the form of the effective interaction has been discussed by Hubbard (1957). Then, in the Gell-Mann-Brueckner approximation,

$$G(rtr'trt''r't'') = G_0(rtrt'')G_0(r'tr't'') - \tfrac{1}{2} G_0(rtr't'')G_0(r'trt'')$$

$$- \int d^4y_1 d^4y_2\ G_0(rty_1)G_0(r'ty_2)V(y_1 - y_2)G_0(y_1 rt'')G_0(y_2 r't'')$$

$$\qquad (2.3.12)$$

$$+ \tfrac{1}{2} \int d^4y_1 d^4y_2\ G_0(rty_1)G_0(r'ty_2)v(y_1 - y_2)G_0(y_1 r't'')G_0(y_2 rt'').$$

We attempt at this stage to evaluate the pair function in the approximation in which we consider the first three terms on the right-hand side of (2.3.12). The first two terms lead to the usual Hartree-Fock result given in §2.1, equation (2.1.6),

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and we write out only the third term explicitly, called G_{BG}
in what follows.   It is most convenient to proceed by Fourier
analysis, and to write

$$G_{BG}(rt\ r'\ t\ rt''\ r'\ t'') = \frac{1}{(2\pi)^4} \int dq\ e^{iq\cdot(r-r')}G_{BG}(qt-t'').$$

$$(2.3.13)$$

If we Fourier transform V and G_0, then the result may be written

$$G_{BG}(q) = \frac{1}{(2\pi)^7} \int dk\ d\varepsilon\ dk'\ d\varepsilon'\ dw\ G_0(k\varepsilon)G_0(k-q,\varepsilon-w)$$

$$V(qw)G_0(k'\varepsilon')G_0(k-q\varepsilon'+w).$$ $$(2.3.14)$$

Introducing the function

$$Q_0(qw) = \frac{1}{2\pi} \int d^3k \int_{-\infty}^{\infty} d\varepsilon\ G_0(q+k\varepsilon+w)G_0(k\varepsilon)$$ $$(2.3.15)$$

as in Dubois (1959) we may simplify (2.3.14) to read

$$G_{BG}(q) = \frac{1}{(2\pi)^4} \int_{-\infty}^{\infty} dw\ \frac{Q_0{}^2(q.w)/\pi^2 k_f q^2}{1 + \frac{Q_0(q.w)}{\pi^2 k_f q^2}}.$$ $$(2.3.16)$$

Numerical evaluation of this correction to the Hartree-Fock pair
function is now in progress.

The method just described may also be applied to the first
order Green's function to yield the first-order density matrix.
Results essentially equivalent to the momentum distribution of
Daniel and Voske are then obtained.

2.4 The meaning of a Fermi surface

The fact that we can obtain the momentum distribution in
two limiting cases has interesting implications. For, as the
work of Daniel and Vosko shows, the discontinuity in P(K) at
the Fermi surface for $r_s = 0$ is not removed but only reduced
as the density is lowered. While this result seems not to
have been established rigorously outside perturbation theory,
there seems strong empirical evidence from the sharpness of
the Fermi surface in real metals that such a discontinuity does
in fact persist. However, our low density treatment $r_s \to \infty$
could equally be made the basis of a perturbation treatment,
and no sign of the discontinuity would then occur. Thus, the
evidence seems clear that as we follow the momentum distribution
as it develops from the two limiting cases of small and large
r_s there must come a critical coupling strength, or a critical
density, at which the discontinuity in the momentum distribution
is reduced to zero. For lower densities, it then appears that
the concept of a Fermi surface will no longer be useful. We
believe at present that the critical value, r_c say, will lie
outside the range of real metallic densities, or in other words
that r_c will exceed 5·5. No quantitative evaluation has so far
proved possible however. Questions also remain as to the nature
and order of the 'transition' occurring at r_c. We do not expect
that the pair function will undergo any marked changes at r_c and
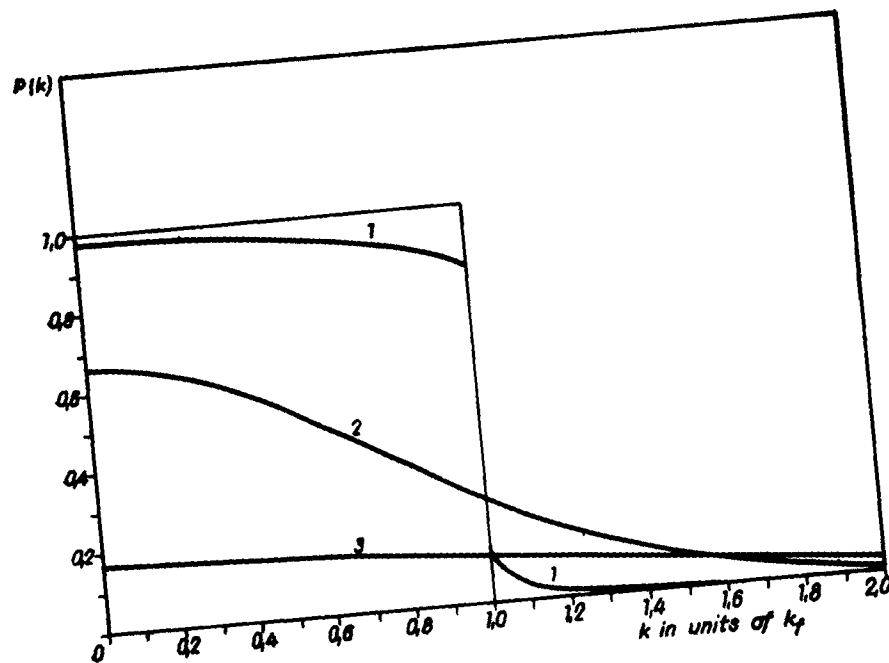
Fig. 2. Momentum distribution in an electron gas
Curve 1. DANIEL and VOSKO results for $r_s = 2$
Curve 2. Low density form for $r_s = 16$
Curve 3. Low density form for $r_s = 100$

probably, to obtain a clear picture of the transition, it will eventually prove necessary to examine the third and higher-order density matrices.

Finally, to give an indication of the change in the momentum distribution as the density is varied, we have plotted in curve 1 of Figure 2 results for $P(K)$ as given by Daniel and Vosko for the high density values ($r_s \not= 2$) and by (2.2.6) for the low density region. Curve 2 for $r_s = 16$ should be viewed with some caution, but the result for $r_s = 100$ (curve 3) should represent a good approximation. The great difficulty, as we have stressed, is to obtain a sufficiently good approximation to the ground state in the region $2 < r_s < 5.5$ and to locate the critical value of r_s with precision.

3. Test of perturbation method for calculating electron momentum distribution (with D. Hilton)

Since the above work was completed, we have been concerned about the possibility that the Daniel and Vosko theory of the momentum distribution of a high density electron gas may not be physically correct. Thus, as they in fact point out, the discontinuity in their momentum distribution may arise from perturbation theory, because it is already present in the zeroth-order problem.

In view of the importance of this question, we have sought a soluable problem in which perturbation methods can be avoided, and yet the electron momentum distribution can still be calculated. It seems to us that there is a problem; not, unfortunately, closely related to the correlation problem; which we can solve exactly, in which a perturbation is applied to an electron gas. This is the case of non-interacting electrons in a magnetic field, and in view of the interest in the momentum distribution calculation by a non-perturbative method, we discuss it in some detail below.

3.1 Bloch matrix and momentum distribution for non-interacting electrons in a magnetic field

As remarked previously, it is fairly clear that a momentum distribution calculated by perturbation theory will contain a discontinuity if the unperturbed solution does so. It is not,

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however, clear that the exact solution will be discontinuous.
In order to investigate the exact solution for the problem of
free non-interacting electrons in the presence of a magnetic
field, we note that the exact Bloch density matrix has been given
by Sondheimer and Wilson (1951) for this case for an infinite
number of particles. It may be written in suitable units (the
magnetic field being in the Z-direction) as

$$C(\underset{\sim}{r}'\ \underset{\sim}{r}\ \beta) = f(\beta)\ \exp[-\frac{iH}{2}\ (x'y - y'x) - \frac{g(\beta)}{4}\ \{(x-x')^2 + (y-y')^2\}$$

$$+ (z-z')^2/4\beta]\qquad\qquad (3.1.1)$$

where

$$g(\beta) = H\ \coth\ H\beta\ \ \text{and}\ \ f(\beta) = \frac{H}{(\pi\beta)^{\frac{1}{2}}}\ \ \text{cosech}\ H\beta.$$

It is easily seen that when the magnetic field H tends to zero,
we recover the field free solution

$$\frac{1}{(\pi\beta)^{\frac{1}{2}}}\ e^{-(r-r')^2/4\beta}\qquad \text{(Note that here the energy is}$$

$$\qquad\qquad\qquad \text{expressed in Rydbergs)}.\qquad (3.1.2)$$

We shall work with the quantity

$$D(\underset{\sim}{k}\ \beta) = \int C(\underset{\sim}{k}\ \underset{\sim}{k}'\ \beta)\ d\underset{\sim}{k}'\qquad\qquad (3.1.3)$$

where

$$C(\underset{\sim}{k}\ \underset{\sim}{k}'\ \beta) = \int e^{i\underset{\sim}{k}'\underset{\sim}{r}}\ e^{-i\underset{\sim}{k}\cdot\underset{\sim}{r}'}\ C(\underset{\sim}{r}\ \underset{\sim}{r}'\ \beta)\ d\underset{\sim}{r}\ d\underset{\sim}{r}'\qquad (3.1.4)$$

Then by use of the relation pointed out by March and Murray (1960)

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$$\rho(\underset{\sim}{r}' \; \underset{\sim}{r} \; \zeta) = \frac{1}{2\pi i} \int_{\sigma-i\infty}^{\sigma+i\infty} e^{\beta\zeta} \; \frac{C(\underset{\sim}{r}' \; \underset{\sim}{r} \; \beta)}{\beta} \; d\beta \qquad (3.1.5)$$

we see that

$$Q(\underset{\sim}{k} \; \zeta) = \int P(\underset{\sim}{k} \; \underset{\sim}{k}' \; \zeta) d\underset{\sim}{k}' = \frac{1}{2\pi i} \int_{\sigma-i\infty}^{\sigma+i\infty} e^{\beta\zeta} \; \frac{D(\underset{\sim}{k} \; \beta)}{\beta} \; d\beta. \qquad (3.1.6)$$

We must remark that it is only in special cases as, for example, when the electrons are free, that $Q(\underset{\sim}{k} \; \zeta)$ is the momentum distribution; we will return to this point later.

If we define the mixed matrix

$$C(\underset{\sim}{k} \; \underset{\sim}{r} \; \beta) = \int e^{i\underset{\sim}{k}\cdot\underset{\sim}{r}'} \; C(\underset{\sim}{r}' \; \underset{\sim}{r} \; \beta) \; d\underset{\sim}{r}' \qquad (3.1.7)$$

it is easily seen that

$$D(\underset{\sim}{k} \; \beta) = C(\underset{\sim}{k} \; \underset{\sim}{r} \; \beta)_{\underset{\sim}{r}=0} \qquad (3.1.8)$$

We perform the transform (3.1.7) by use of the formula

$$\int_{-\infty}^{+\infty} e^{-tx^2+2\eta x} dx = \sqrt{\frac{\pi}{t}} \; e^{\eta^2/t}, \quad \text{Re } t > 0 \qquad (3.1.9)$$

and find that

$$C(\underset{\sim}{k} \; \underset{\sim}{r} \; \beta) = \beta^{\frac{1}{2}} \frac{f(\beta)}{g(\beta)} \, e^{-\beta k_z^2} \, e^{-(k_x^2+k_y^2)/g} \, e^{-H^2/4g(x^2+y^2)} \, e^{H(k_x y - k_y x)} \, e^{i\underset{\sim}{k}\cdot\underset{\sim}{r}}$$

$$(3.1.10)$$

or

$$D(\underset{\sim}{k} \; \beta) = \frac{1}{\cosh H\beta} \, e^{-\beta k_z^2} \, e^{-(k_x^2+k_y^2)/g}. \qquad (3.1.11)$$

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Now $\quad \dfrac{1}{g} = \dfrac{\tanh H\beta}{H} \to \beta \quad$ as $\quad H \to 0$, and

$$\lim_{H \to 0} \cosh H\,\beta = 1, \text{ so that}$$

$$\lim_{H \to 0} D(\underset{\sim}{k}\ \beta) = e^{-\beta k^2},$$

which is the correct answer. For we have for the momentum distribution in this case

$$Q(\underset{\sim}{k}\ \zeta) = \frac{1}{2\pi i} \int_{\sigma - i\infty}^{\sigma + i\infty} \frac{e^{-\beta k^2}}{\beta}\ e^{\beta \zeta}\ d\beta. \qquad (3.1.12)$$

When $k^2 > \zeta$ we close the contour by a semi-circle at infinity in the right half-plane. The integrand vanishes in this semi-circle, and since no singularities are enclosed the $R(\underset{\sim}{k}\ \zeta)$ vanishes. On the other hand if $k^2 < \zeta$, the integrand vanishes in a semi-circle at infinity in the left-half plane. However the contour now encloses the singularity residue 1 at the origin. Thus

$$Q(\underset{\sim}{k}\ \zeta) = \frac{1}{2\pi i} \int_{\sigma - i\infty}^{\sigma + i\infty} \frac{e^{-\beta k^2}}{\beta}\ e^{\beta \zeta}\ d\beta = \begin{matrix} 1 & k^2 < \zeta \\ 0 & k^2 > \zeta \end{matrix}, \qquad (3.1.13)$$

the correct result for non-interacting electrons in the absence of a magnetic field.

When the magnetic field is not zero, we have

$$Q(\underline{k}) = \int P(\underline{k}\ \underline{k}')d\underline{k}' = \frac{1}{2\pi i} \int_{\sigma-i\infty}^{\sigma+i\infty} \frac{e^{-\beta(k_z^2-\zeta)}\ e^{-(k_x^2+k_y^2)/g(\beta)}}{\beta \cosh H\beta}\ d\beta$$

$$= \frac{1}{2\pi i} \int_{\sigma-i\infty}^{\sigma+i\infty} 2\ \frac{e^{\beta(\zeta-k_z^2-H)}\ e^{-(k_x^2+k_y^2)/g(\beta)}}{\beta(1 - e^{-2H\beta})}\ d\beta. \qquad (3.1.14)$$

Again we close the contour by a semi-circle at infinity in the right half plane. The integrand vanishes on this semi-circle if

$$\zeta - k_z^2 - H < 0.$$

Thus

$$Q(\underline{k}\ \zeta) = 0 \qquad \text{if} \qquad k_z^2 + H > \zeta. \qquad (3.1.15)$$

This result is at first sight a little surprising: we would expect the discontinuity to persist in the z-direction, we might also expect it to remain in the same place, i.e. $k_z^2 = \zeta$ when $k_x^2 + k_y^2 = 0$, for the longitudinal motions of the electrons are unaffected by a magnetic field. However, the result may be explained by supposing electrons originally moving wholly in the z-direction (that of the magnetic field) to jump into states energetically more favourable and for which there are non-zero components or momentum in directions transverse to the magnetic field.

Evaluation of the integral (3.1.14) does not seem possible when the equality in equation (3.1.15) does not hold, for there are essential singularities of the integrand on the imaginary axis.

We are thus compelled to proceed as follows. We put

$$\xi = \xi' - k_z^2 - H; \qquad \eta = (k_x^2 + k_y^2)/H.$$

We now have

$$\frac{1}{2\pi i} \int_{\sigma - i\infty}^{\sigma + i\infty} \frac{e^{\beta \xi} e^{-\eta \tan H\beta}}{\beta(1 - e^{-2H\beta})} \, d\beta = \frac{1}{2\pi} \int_{-\infty}^{+\infty} \frac{e^{\xi(\sigma + it)} e^{-\eta \tan(t + i\sigma)}}{(\sigma + it)(1 - e^{-2H(\sigma + it)})} \, dt,$$

(3.1.16)

and we will attempt to prove this function continuous as a function
of η by showing that its derivative with respect to η exists and
is finite everywhere.   To do so we take the derivative under the
integral sign.   It may be noted that we have already interchanged
orders of integration: we have taken a Fourier transform before
the inverse Laplace transform.   However, in that case, there is
less apparent danger than here, where we seek to prove the
derivative always bounded;   for we must guarantee that if the
transform of the derivative is bounded, then so is the derivative
of the transform.   We give an argument to justify our procedure
which can also be used, with the necessary changes, to justify
changes of order of integration.

We note that the relation

$$\int_0^\infty \rho(\xi \, \eta \, \zeta) e^{-\beta \zeta} \, d\zeta = \frac{1}{\beta} C(\xi \, \eta \, \beta) \qquad (3.1.17)$$

can be made rigorous when C is a Dirichlet series;   when there
is a finite number of particles, and the energy spectrum discrete.
We have the functions of the form

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$$\rho(\xi \ \eta \ \zeta) = \sum_1 V_1(\xi \ \eta) \ H(E_1 \ \zeta), \qquad (3.1.18)$$

$$C(\xi \ \eta \ \beta) = \sum_1 V_1(\xi \ \eta) e^{-\beta E_1}. \qquad (3.1.19)$$

$$H(E_1 \ \zeta) = \begin{matrix} 1 & E_1 < \zeta \\ 0 & E_1 > \zeta \end{matrix}. \qquad (3.1.20)$$

(The E_1 are the one-particle energy levels).

Now when there is a finite number of particles, the allowed values of momenta (and so ζ and η) form a discrete set. We must take finite differences:

$$\Delta\rho = \frac{\rho(\xi \ \eta + h \ \zeta) - \rho(\xi \ \eta + \zeta)}{h}. \qquad (3.1.21)$$

and obviously

$$\int_0^\infty \Delta\rho \ e^{-\beta \zeta} \ d\zeta = \Delta C/\beta. \qquad (3.1.22)$$

Now having passed to the limit of an infinite number of particles, we have a quasi-continuous function in η, the limit of the sets of functions obtained by joining neighbouring allowed values of η by straight lines. For such a function, say P, the derivative is well approximated to be the finite difference of ρ for a finite but very large number of particles, i.e. if

$$\rho_L = \lim_{N\to\infty} \rho_N, \qquad N \text{ the number of particles,}$$

$$\frac{dP_L}{d\eta} = \lim_{N\to\infty} \Delta\rho_N.$$

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Such considerations must hold for both sides of equation (3.1.22).
Thus

$$\int_0^\infty \frac{d\rho_L}{d\eta} e^{-\beta\zeta} d\zeta = \frac{dC_L}{d\eta} / \beta.$$

Our problem now consists of proving the boundedness of

$$\int_{-\infty}^{+\infty} \frac{e^{i\xi t} \tan H(i\sigma+t) e^{-\eta} \tan(i\sigma+t)}{(\sigma+it)(1 - e^{-2H(\sigma+it)})} dt. \qquad (3.1.23)$$

We will use the second mean value theorem, which states that if
$\phi(x)$ is a monotonic function, and $f(x)$ any other function, then

$$\int_a^b \phi(x)f(x)dx = \phi(a) \int_a^\xi f(x)dx + \phi(b) \int_\xi^b f(x)dx, \quad a < \xi < b. \qquad (3.1.24)$$

Let us apply this theorem to the integral

$$I = \frac{1}{2\pi i} \int_{\sigma-i\infty}^{\sigma+i\infty} \frac{f(\beta)}{\beta} d\beta,$$ where $f(\beta)$ is periodic on the contour of integration, and has a finite mean value m.

We write

$$f(\beta) = m + g(\beta). \qquad \text{Then}$$

$$I = \frac{m}{2} + \frac{1}{2\pi i} \int_{\sigma-i\infty}^{\sigma+i\infty} \frac{g(\beta)}{\beta} d\beta = \frac{m}{2} + \frac{1}{2\pi} \int_{-\infty}^{+\infty} \frac{g(\sigma+it)}{(\sigma+it)} dt. \qquad (3.1.25)$$

It is now sufficient to consider

$$\int_0^a \frac{g(\sigma+it)}{\sigma+it}$$ and to show that it has an upper bound independent of a (we let $a \to \infty$).

We put

$$\frac{1}{\sigma + it} = \frac{\sigma}{\sigma^2 + t^2} - \frac{it}{\sigma^2 + t^2}.$$

We then see that the real part is monotonic and (3.1.24) can be applied immediately:

$$\sigma \int_0^a \frac{g(\sigma + it)}{\sigma^2 + t^2} dt = \frac{1}{\sigma} \int_0^{\xi(a)} g(\sigma + it)dt + \frac{\sigma}{\sigma^2 + a^2} \int_{\xi(a)}^a g(\sigma + it)dt. \quad (3.1.26)$$

Since $g(\sigma + it)$ is periodic in t with mean value zero, we see that the two integrals on the right are bounded and as a $\rightarrow \infty$ the second term on the right hand side goes to zero so that the upper bound for the left hand side is independent of a for a very large. The fact that ξ depends on a does not affect the argument because in the first integral of the right hand side, we can simply choose $\xi(a)$ to make the integral a maximum, to obtain an upper bound. It can be shown also that $\xi(a)$ tends to a constant as a $\rightarrow \infty$. As for the imaginary part of $\frac{1}{\sigma + it}$, we write

$$\int_0^a \frac{t}{\sigma^2 + t^2} g(\sigma + it)dt = \int_0^x \frac{g(\sigma + it)t}{\sigma^2 + t^2} dt + \int_x^a \frac{g(\sigma + it)t}{\sigma^2 + t^2} dt \quad (3.1.27)$$

where x is chosen such that $\frac{t}{\sigma^2 + t^2}$ is monotonic in the interval (x, a). The first integral on the right hand side is obviously finite and is independent of a, and the second integral may be treated as before.

We have thus shown that if $f(\beta)$ is bounded and periodic on the contour of integration, the integral

$$\frac{1}{2\pi i} \int_{\sigma - i\infty}^{\sigma + i\infty} \frac{f(\beta)}{\beta} d\beta \qquad \text{is bounded.}$$

We apply these observations to the integral (3.1.23). There

is a product of two periodic functions in the integrand. The period of one depends on ζ, and the period of the other on H. The periods of both are independent of η. The product will be periodic if ξ is adjusted such that the ratio of the two periods is rational. It is therefore possible to state that:

For every value of ξ such that ξ/H is a rational number, the derivative of $Q(\underset{\sim}{k} \zeta)$ with respect to η is bounded; i.e. for such values of ξ, $Q(\underset{\sim}{k})$ has no discontinuities as a function of k_x and k_y.

We note that we can approach any point ξ, with a ξ obeying the condition expressed in the last statement as close as we please.

3.2 Difficulties of direct use of double Fourier transform of Bloch matrix

Inspection of equation (3.1.10) makes it clear that the second Fourier transform may be carried out by use of (3.1.9) and one might therefore inquire why we have not simply carried out the second transform instead of working with the quantity $D(\underset{\sim}{k}, \beta)$. The reason will now become clear, for we will examine the consequence of such a procedure.

We note that Sondheimer and Wilson's expression is of the form

$$C(\underset{\sim}{r}_1 \ \underset{\sim}{r}_2 \ \beta) = f(H \cdot \underset{\sim}{r}_1 \ x \underset{\sim}{r}_2) \ \Theta(\underset{\sim}{r}_1 - \underset{\sim}{r}_2 \ \beta) \quad (\underset{\sim}{H} = H \ \hat{\underset{\sim}{z}}). \qquad (3.2.1)$$

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f is independent of β, so that on performing the inverse transform we obtain

$$\rho(r_1 r_2 \zeta) = f(\underset{\sim}{H} \cdot \underset{\sim}{r}_1 \times \underset{\sim}{r}_2) \, g(\underset{\sim}{r}_1 - \underset{\sim}{r}_2 \zeta). \qquad (3.2.2)$$

Now the momentum distribution is the diagonal element of

$$P(\underset{\sim}{k}_1 \underset{\sim}{k}_2) = \int \rho(\underset{\sim}{r}_1 \underset{\sim}{r}_2) \, e^{-i\underset{\sim}{k}_1 \underset{\sim}{r}_1} \, e^{i\underset{\sim}{k}_2 \underset{\sim}{r}_2} \, d\underset{\sim}{r}_1 \, d\underset{\sim}{r}_2 \qquad (3.2.3)$$

We put

$$g(\underset{\sim}{r}_1 - \underset{\sim}{r}_2) = \int Q(\underset{\sim}{k}) \, e^{i\underset{\sim}{k} \cdot (\underset{\sim}{r}_1 - \underset{\sim}{r}_2)} \, d\underset{\sim}{k}. \qquad (3.2.4)$$

Then

$$P(\underset{\sim}{k}_1 \underset{\sim}{k}_2) = \int d\underset{\sim}{r}_1 \, d\underset{\sim}{r}_2 \, f(\underset{\sim}{H} \, \underset{\sim}{r}_1 \times \underset{\sim}{r}_2) \int d\underset{\sim}{k} \cdot e^{-i(\underset{\sim}{k}_1 - \underset{\sim}{k}) \cdot \underset{\sim}{r}_1} \, e^{i(\underset{\sim}{k}_2 - \underset{\sim}{k}) \cdot \underset{\sim}{r}_2} \, Q(\underset{\sim}{k})$$

$$= \int F(\underset{\sim}{k}_1 + \underset{\sim}{k} \, \underset{\sim}{k}_2 + \underset{\sim}{k}) \, Q(\underset{\sim}{k}) \, d\underset{\sim}{k}, \qquad (3.2.5)$$

where

$$F(\underset{\sim}{k}_1 \underset{\sim}{k}_2) = \int f \, e^{-i\underset{\sim}{k}_1 \underset{\sim}{r}_1} \, e^{i\underset{\sim}{k}_2 \cdot \underset{\sim}{r}_2} \, d\underset{\sim}{r}_1 \, d\underset{\sim}{r}_2 \qquad (3.2.6)$$

It can easily be shown that the diagonal element of the double Fourier transform of a function of the form $F(\underset{\sim}{H} \cdot \underset{\sim}{r}_1 \times \underset{\sim}{r}_2)$ is independent of k_x and k_y :

$$F(\underset{\sim}{k} \, \underset{\sim}{k}) = C \, \delta(k_z) \, \delta(k_z), \quad \text{where C is some constant.}$$

We therefore obtain

$$P(\underset{\sim}{k} \, \underset{\sim}{k}) = \delta(\underset{\sim}{k}) C \int Q(k_x \, k_y \, k_z) \, dk_x \, dk_y; \quad \text{C some constant.}$$

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[The δ-function appears since we have taken a double Fourier transform and so obtained the momentum distribution for all electrons, and there are an infinite number of them.]

The resulting momentum distribution is constant in the k_x and k_y directions. This is obviously physically incorrect.

We must expect that when magnitude of the magnetic field is very small, the true momentum distribution approximates closely to that of the electrons in the absence of the magnetic field. How are we to explain this peculiarity of the Sondheimer and Wilson solution?

We think the answer is as follows. Sondheimer and Wilson avoid the troubles earlier workers encountered with boundary conditions by working, not with a finite system, but with an infinite one. They obtain the solution of the Bloch equation

$$H_{\underset{\sim}{r}} \, C(\underset{\sim}{r}' \; \underset{\sim}{r} \; \beta) + \frac{\partial C}{\partial \beta} \, (\underset{\sim}{r}' \; \underset{\sim}{r} \; \beta) = 0 \qquad (3.2.7)$$

with boundary condition

$$C(\underset{\sim}{r}' \; \underset{\sim}{r} \; 0) = \delta(\underset{\sim}{r}' - \underset{\sim}{r}) \qquad (3.2.8)$$

(H is the Hamiltonian)

and there can be no doubt that their solution is correct for the infinite system. However, supposing $C_N(\underset{\sim}{r}' \; \underset{\sim}{r} \; \beta)$ is the Bloch matrix for N-particles, the momentum distribution in the limit as N→∞ is the inverse Laplace transform of

$$\frac{C(\underset{\sim}{k} \, \underset{\sim}{k} \, \beta)}{\beta} = \frac{1}{\beta} \lim_{N \to \infty} \int_{\substack{\text{Volume of} \\ \text{system}}} C_N(\underset{\sim}{r}' \, \underset{\sim}{r} \, \beta) e^{-i\underset{\sim}{k} \cdot \underset{\sim}{r}'} \, e^{i\underset{\sim}{k} \cdot \underset{\sim}{r}} \, d\underset{\sim}{r} \, d\underset{\sim}{r}'. \qquad (3.2.9)$$

In taking a double Fourier transform of the S-W solution we have reversed order of integration and limiting process, and this appears to be the reason why we obtain an unphysical answer. (It should be noticed that the limiting process here is of a different nature to the one we make on equation (3.1.22). Here limits of integration vary as we vary the number of particles).

In working with the mixed matrix $C(\underset{\sim}{k} \, \underset{\sim}{r} \, \beta)$ we have avoided these difficulties. Analogous to (3.2.7), the mixed matrix obeys the equation

$$H_{\underset{\sim}{r}} \, C(\underset{\sim}{k} | \underset{\sim}{r} \, \beta) + \frac{\partial C}{\partial \beta} \, (\underset{\sim}{k} | \underset{\sim}{r} \, \beta) = 0 \qquad (3.2.10)$$

with boundary condition

$$C(\underset{\sim}{k} | \underset{\sim}{r} \, 0) = e^{i\underset{\sim}{k} \cdot \underset{\sim}{r}} , \qquad (3.2.11)$$

and it can be readily verified that the quantity defined by equation (3.1.10) satisfies equations (3.2.10) and (3.2.11).

3.3 Relation to Van Hove's conjecture on use of perturbation theory

In concluding this discussion, we shall refer to a conjecture by Van Hove (1959) which has only recently come to our attention. Van Hove has suggested that whereas it is known that with

attractive potentials the zeroth order Fermi distribution cannot be used to generate tne correct solution when the interactions are switched on, the same might also be true for repulsive interactions.

While we are not able to draw a decisive conclusion about the correlation problem from our work above, we can say with certainty that in the k_x and k_y directions the momentum distribution does not have a discontinuity. However, while we note that, if generated by perturbation theory, we can expect such a discontinuity to be preserved, it should be pointed out that the perturbative treatment leads to a pathological result in this case. We do feel however that our ability to carry through the calculation of the momentum distribution exactly in this case is of considerable theoretical interest. We are also of the opinion that the result may have practical significance and we are at present planning the numerical calculation of the momentum distribution in the presence of a magnetic field. Compton effect studies or positron annihilation experiments in the presence of a magnetic field may prove illuminating in the future.

4. Variational second-order density matrices built from two-body orbitals

We have so far discussed chiefly the extreme limits of weak and strong coupling. Unfortunately, the methods used there are not adequate for the range of intermediate coupling, and we therefore turn our attention at this point to more general consideration of the form of the second-order density matrix. All evidence seems to us to point to the fact that this quantity affords the best available tool for dealing with many-body problems in which only two-body forces operate.

4.1 Discussion of necessary and sufficient conditions for variational validity of second-order density matrices

In this section we shall formulate necessary and sufficient conditions such that a many-body wave function expanded in terms of orthonormal two-body orbitals $\{\phi_\ell \, (r_1 r_2)\}$ shall be antisymmetric. These in particular provide necessary conditions that the type of second order density matrix suggested by Young and March (1960), viz:

$$\Gamma(\underset{\sim}{r}_1' \underset{\sim}{r}_2' \mid \underset{\sim}{r}_1 \underset{\sim}{r}_2) = \sum_{\ell=1}^{N(2N-1)} \phi_\ell^{\ast} \, (\underset{\sim}{r}_1' \underset{\sim}{r}_2') \, \phi_\ell (\underset{\sim}{r}_1, \, \underset{\sim}{r}_2) \qquad (4.1.1)$$

(where 2N is the number of particles) shall be derivable from an antisymmetric many body wave function. In §4.3 it will be shown that with the particular form of orbitals chosen by Young and March in method (B) of their paper (which method is at first sight the more promising of the two they propose, since it reduces to the correct Hartree-Fock solution in the high density limit) the conditions cannot be satisfied, at least in one dimension.

We will also discuss the question of the sufficiency of the conditions on the orthonormal orbitals $\{\phi_\ell(\underset{\sim}{r}_1 \underset{\sim}{r}_2)\}$ for density matrices of the type displayed in equation (4.1.1) to be derivable from an antisymmetric wave function. The sufficiency follows from an assertion by Bopp (1959), of which Coleman (unpublished work; 1961) has questioned the validity and has claimed to have

produced a counter example. Both the lacuna in Bopp's argument
and Coleman's counter-example will be examined in §4.2.

We take a complete set of two-body orthornormal orbitals
(to be referred to as geminals) $\{\psi_\ell(\underline{x}_1\underline{x}_2)\}$ and expand the
antisymmetric wave function for 2N particles in terms of them:

$$\Psi(\underline{x}_1\underline{x}_2..\underline{x}_{2N}) = \sum_{\ell_1..\ell_N} C_{\ell_1\ell_2..\ell_N} \psi_{\ell_1}(\underline{x}_1\underline{x}_2)\psi_{\ell_2}(\underline{x}_3\underline{x}_4)...\psi_{\ell_N}(\underline{x}_{2N-1}\underline{x}_{2N})$$

$$(4.1.2)$$

$C_{\ell_1\ell_2..\ell_N}$ must be invariant under permutation of $\ell_1...\ell_N$ and
also

$$\sum_{\ell_1..\ell_N} \left|C_{\ell_1..\ell_N}\right|^2 = 1$$

The second order density matrix is

$$\Gamma(\underline{x}_1'\underline{x}_2'|\underline{x}_1\underline{x}_2) = \sum_{\ell'\ell} a_{\ell'\ell} \psi_{\ell'}^{\ast}(\underline{x}_1\underline{x}_2)\psi_{\ell}(\underline{x}_1\underline{x}_2), \qquad (4.1.3)$$

$$\sum_{\ell} a_{\ell\ell} = N(2N - 1), \qquad (4.1.4)$$

where

$$a_{\ell'\ell} = N(2N - 1) \sum_{\ell_2..\ell_N} C_{\ell'\ell_2..\ell_N}^{\ast} C_{\ell\ell_2..\ell_N}.$$

One can see that $a_{\ell'\ell} = a_{\ell\ell'}^{\ast}$ - the matrix $(a_{\ell'\ell})$ is Hermitian;
it is thus diagonalisable and there exis geminals $\{\phi_\ell(\underline{x}_1\underline{x}_2)\}$,

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which we shall call natural geminals, such that

$$\Gamma(\underline{x}_1'\underline{x}_2'|\underline{x}_1\underline{x}_2) = \sum_{\ell} b_\ell \, \phi_\ell^{\mathbf{x}}(\underline{x}_1'\underline{x}_2') \, \phi_\ell(\underline{x}_1\underline{x}_2) \qquad (4.1.5)$$

Now the antisymmetry requirement

$$\Psi(\underline{x}_1\underline{x}_2\cdot\cdot\underline{x}_{2N}) = -\Psi(\underline{x}_2\underline{x}_1\cdot\cdot\underline{x}_{2N})$$

implies that

$$\sum_{\ell_1} c_{\ell_1\ell_2\cdot\cdot\ell_N}\{\psi_\ell(\underline{x}_1\underline{x}_2) + \psi_{\ell_2}(\underline{x}_2\underline{x}_1)\} = 0 \quad (\text{all } \ell_2,\ell_3,\cdot\cdot\ell_N) \qquad (4.1.6)$$

and the requirement

$$\Psi(\underline{x}_1\underline{x}_2\underline{x}_3\underline{x}_4\ldots) = -\Psi(\underline{x}_1\underline{x}_3\underline{x}_2\underline{x}_4\ldots)$$

implies that

$$\sum_{\ell_1\ell_2} c_{\ell_1\ell_2\ell_3\ldots\ell_N}\{\psi_{\ell_1}(\underline{x}_1\underline{x}_2)\psi_{\ell_2}(\underline{x}_3\underline{x}_4) + \psi_{\ell_1}(\underline{x}_1\underline{x}_3)\psi_{\ell_2}(\underline{x}_2\underline{x}_4)\} = 0$$

$$(\text{all } \ell_3,\ldots,\ell_N) \quad (4.1.7)$$

Equations (4.1.6) and (4.1.7) are necessary and sufficient
conditions that the expansion in equation (4.1.2) is an allowable
many-body wave function.   If the expansion is in terms of the
natural geminals, equation (4.1.6) is replaced by

$$\phi_\ell(\underline{x}_1\underline{x}_2) = -\phi_\ell(\underline{x}_2\underline{x}_1) \qquad (\text{all } \ell). \qquad (4.1.8)$$

Let us now consider a density matrix formed from a finite
number of geminals,

$$\Gamma(\underline{x}_1'\underline{x}_2'|\underline{x}_1\underline{x}_2) = \sum_{\ell'\ell}^{(K)} a_{\ell'\ell} \, \psi_{\ell'}^{\mathbf{x}}(\underline{x}_1'\underline{x}_2')\psi_\ell(\underline{x}_1\underline{x}_2). \qquad (4.1.9)$$

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The same orbitals, and no others orthogonal to them appear
in the wave function, since we have

$$\sum_{\ell_2..\ell_N} \left| C_{\ell_1 \ell_2 .. \ell_N} \right|^2 = 0, \qquad \ell_1 > K.$$

Hence

$$\Psi(\underline{r}_1 \underline{r}_2 ... \underline{r}_{2N}) = \sum_{\ell_1 .. \ell_N}^{(K)} C_{\ell_1 .. \ell_N} \, \Psi_{\ell_1}(\underline{r}_1 \underline{r}_2) .... \Psi_{\ell_N}(\underline{r}_{2N-1} \underline{r}_{2N}) \qquad (4.1.10)$$

Conditions (4.1.6) and (4.1.7), where now there is an upper
limit K on the summations, form necessary conditions that we can
choose a matrix of the form (4.1.9). For particular choice of
$a_{\ell'\ell}$, however, the conditions are not proved to be sufficient.
In particular, if we take $N(2N - 1)$ antisymmetric orbitals and
prove that an antisymmetric wave function for 2N particles may
be expanded wholly in terms of them, we have still not proved
that these orbitals are natural geminals and so the density
matrix is of the Young-March form (equation (4.1.1)).

However, Bopp (1959) states that there is an upper bound
to the $a_{\ell\ell}$:

$$0 \leqslant a_{\ell\ell} \leqslant 1 \qquad (4.1.11)$$

If equation (4.1.11) is true, then it is easily seen that the
second order density matrix for an antisymmetric wave function
formed from $N(2N - 1)$ geminals must be of the Young-March form.

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However, equation (4.1.11) is not established beyond doubt, and thus will now be discussed.

4.2 Bopp's assertion and Coleman's counter example

Referring to the expansion of the second order density matrix in terms of natural geminals, (equation (4.1.5)) it can readily be shown that if

$$0 < b_\ell < 1, \tag{4.2.1}$$

then this also holds for the diagonal elements of the matrix in any other representation (that is, equation (4.1.11) is also true).

Let us write the many body wave function as

$$\Psi = \sum_n \phi_n \sum_K c_K{}^n U_K{}^{(n)} \tag{4.2.2}$$

where $\{\phi_n\}$ is the set of natural geminals,

$$U_K{}^{(n)} = \prod_{i=3}^{2N} U_{k_i}{}^{(n)} (i) \quad \text{(K labelling the configuration } k_3 \ldots k_{2N}$$

and the $U_k{}^{(n)}$ are orthonormal and defined by the integral equation

$$\int \phi_n (13) \, \phi(23) \, U_k{}^{(n)}(2) \, d(23) = \lambda_k{}^{(n)} \, U_k{}^{(n)} (1).$$

We now antisymmetize $U_k{}^{(n)}$ and so form a normalised determinant $D_k{}^{(n)}$ (3...2N) by which we replace $U_k{}^{(n)}$ in equation (4.2.2).

We now have a product

$$\phi_n (12) \, D_k{}^{(n)} (3..2N). \quad \text{We antisymmetize this}$$

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and again normalise, obtaining a function

$$X_K^{(n)} \quad (1,2,\ldots,2N).$$

Now Bopp gives an upper bound for the b_n:

$$b_n \leqslant \sum_K | < \psi \; X_K^{(n)} > |^2 \qquad (4.2.3)$$

which he replaces by

$$b_n \leqslant 1.$$

It is easily seen that this last equation immediately follows
if

$$< X_{k_1} \; X_{k_2} > = \delta_{k_1 k_2}. \qquad (4.2.4)$$

It can be shown that

$$\phi_n(12) = \sum_{\ell m} \alpha_{\ell m} \; U_\ell^{(n)} \; (1) \; U_m^{(n)} \; (2) \qquad (4.2.5)$$

where $\quad \alpha_{\ell\ell} = 0$

and if $\quad \alpha_{\ell m} \neq 0, \quad$ then

$$\left.\begin{array}{l} \alpha_{\ell p} = 0 \quad \text{all } p \neq m \\[4pt] \alpha_{qm} = 0 \quad \text{all } q \neq \ell. \end{array}\right\} \qquad (4.2.6)$$

Thus apart from a normalisation factor X_K is equal to

$$\sum_p \ell_p P \sum_{\ell m} \alpha_{\ell m} \; U_\ell^{(n)} \; (1) \; U_m^{(n)} \; (2) \; U_{k_3} \; (3) \; \ldots \; U_{k_{2N}}(2N) \qquad (4.2.7)$$

Consider a second function X_κ. This is,

$$\sum_p \zeta_p P \sum_{\ell m} \alpha_{\ell m} \; U_\ell^{(n)} \; (1) \; U_m^{(n)} \; (2) \; U_{\kappa_3} \; (3) \; \ldots \; U_{\kappa_{2N}}(2N). \qquad (4.2.8)$$

where $\sum_{p} \zeta_p P$ is the antisymmetrization operator.

Now if the products $\prod_{k_1=3} U_{k_1}{}^{(n)}$ and $\prod_{\kappa_1=3} U_{\kappa_1}{}^{(n)}$

differ by more than two functions $U_k{}^{(n)}$, it is easy to see that

$$< X_K{}^x X_\kappa > = 0 \qquad (4.2.9)$$

Also, if the two products only differ by one function then by condition (4.2.6) equation (4.2.9) again holds.

However, if the products differ by just two functions, say

$$U_{\kappa_3}(3) \neq U_{k_3}(3)$$

$$U_{\kappa_4}(4) \neq U_{k_4}(4)$$

then $< X_K{}^x X_\kappa >$ can be seen to be proportional to

$$\alpha^x{}_{\kappa_3 \kappa_4} \; \alpha^x{}_{k_3 k_4} + \alpha^x{}_{k_3 k_4} \; \alpha_{\kappa_3 \kappa_4}$$

This expression will usually be zero because of condition (4.2.6), but not always. Thus equation (4.2.1) does not immediately follow from equation (4.2.3), and in fact Coleman claims a counter example to equation (4.2.1) which we now examine. First we derive the expression for the upper bound for b_n which Coleman uses, examining the conditions carefully.

Let $\{Q_n\}$ be a set of geminals, and expand the wave function as

$$\Psi(12 \ldots M) = \sum_{n} C_n \; \phi_n (12) \; \chi_n(34 \ldots M) \qquad (M = 2N) \qquad (4.2.10)$$

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with $\qquad < \phi_m^{\,z} \phi_n > = \delta_{mn},$ $\qquad < \chi_n^{\,z} \chi_n > = 1,$
and if

$\qquad < \chi_m \chi_n > = \delta_{mn},$ $\qquad$ the ϕ_n are the natural geminals.

The density matrix is

$$\Gamma(1'2'|12) = \sum_{mn} c_n^{\,z} c_n \phi_m(1'2') \phi_n(12) < \chi_m^{\,z} \chi_n >$$

Thus if and only if the ϕ_n are natural geminals,

$$a_{nn} = |c_n|^2 \frac{M}{2}(M - 1).$$

We may then derive an upper bound for $a_{nn} = b_n$:

$$b_n = |c_n|^2 = |< \phi_n(12)\chi_n(3..M)| \Psi(12..M) >|^2$$

$$= |< \phi_n \chi_n|A|\Psi >|^2$$

$\qquad$ (A being the normalised antisymmetrization operator for M particles). This is also

$$\frac{2 b_n}{M(M - 1)} = |< \Psi|A|\phi_n \chi_n >|^2 \leqslant < \phi_n \chi_n|A|\phi_n \chi_n)$$

The equality will only hold provided

$$\Psi \propto A\{\phi_n \chi_n\}.$$

Now Coleman takes a 4-particle wave function of the form

$\qquad \Psi(1234) = \mu A\{\phi(12)\phi(34)\}.$ (μ some normalisation constant)

and shows that with a suitable choice of orbital $\phi(12)$,

$\qquad < \phi(12) \phi(34)|A|\phi(12) \phi(34) >$

can be made arbitrarily close to $1/3$, where Bopp's upper bound is $1/6$.

However, we have remarked that the bound for a_{nn} only holds if ϕ_n is a natural geminal, and this is what Coleman must assume for his counter example to be valid. However, he fails to prove that the orbitals he chooses are natural geminals, and without such a proof his counter example cannot be accepted.

We therefore conclude by remarking that neither condition (4.2.1) nor Coleman's counter example is beyond doubt, so that we cannot provide conditions which we definitely know to be sufficient for the variational validity of matrices of the form suggested by Young and March. In view of the suggestive and promising nature of the form expressed in equation (4.1.1), further work in this direction would obviously be valuable.

4.3 Two Body Bloch Orbitals

To introduce the Wigner lattice of the low density limit we will take the two body functions to be

$$\psi_{k_1 k_2}(r_1 r_2) = \sum_{K_m, K_n} v(k_1 + K_m | k_2 + K_n) \, e^{i(k_1 + K_m) \cdot r_1} \, e^{i(k_2 + K_n) \cdot r_2} \tag{4.3.1}$$

where the K_m are reciprocal lattice vectors.

When the number of particles becomes very large, the many body wave function $\Psi(r_1 r_2 .. r_M)$ is approximated to by

$$\int_{\Omega_B} dk_1 dk_2 ... dk_M \, C(k_1 k_2 | k_3 k_4 | .. k_{M-1} k_M) \psi_{k_1 k_2}(r_1 r_2) ... \psi_{k_{M-1} k_M}(r_{M-1} r_M) \tag{4.3.2}$$

(Ω_B is the volume of the Brillouin zone).

Now we must antisymmetrize in r_1 and r_2, etc. We can do this
by making

$$C(k_1 k_2 | \ldots) = - C(k_2 k_1 | \ldots) \qquad (4.3.3)$$

(here and below the unspecified indices are assumed to take any
value, provided we impose the condition

$$v(k_1 | k_2) = v(k_2 | k_1) \qquad (4.3.4)$$

Equation (4.1.7) becomes

$$\sum_{\substack{K_m K_n \\ K_\mu K_\nu}} \int_{\Omega_B} dk_1 dk_2 dk_3 dk_4 \; C(k_1 k_2 | k_3 k_4 | ..) v(k_1 + K_m | k_2 + K_n) v(k_3 + K_\mu | k_4 + K_\nu) \times$$
$$e^{i(k_1 + K_m) \cdot r_1} e^{i(k_2 + K_n) \cdot r_2} e^{i(k_3 + K_\mu) \cdot r_3} e^{i(k_4 + K_\nu) \cdot r_4}$$

$$=$$

$$\sum_{\substack{K_m K_n \\ K_\mu K_\nu}} \int_{\Omega_B} dk_1 dk_2 dk_3 dk_4 \; C(k_1 k_2 | k_3 k_4 | ,.) v(k_1 + K_m | k_2 + K_n) v(k_3 + K_\mu | k_4 + K_\nu) \times$$
$$e^{i(k_1 + K_m) \cdot r_1} e^{i(k_2 + K_n) \cdot r_3} e^{i(k_3 + K_\mu) \cdot r_2} e^{i(k_4 + K_\nu) \cdot r_4}$$

Multiplying both sides by $e^{-i(\kappa_1 + K_a) \cdot r_1} e^{-i(\kappa_2 + K_b) \cdot r_2} e^{-i(\kappa_3 + K_\alpha) \cdot r_3}$
$\times \; e^{-i(\kappa_4 + K_\beta) \cdot r_4}$ and integrating over all space, we obtain
δ-functions, giving

$$C(\kappa_1 \kappa_2 | \kappa_3 \kappa_4 | ..) v(\kappa_1 + K_a | \kappa_2 + K_b) v(\kappa_3 + K_\alpha | \kappa_4 + K_\beta)$$

$$= - C(\kappa_1 \kappa_3 | \kappa_2 \kappa_4 | ..) v(\kappa_1 + K_a | \kappa_3 + K_\alpha) v(\kappa_2 + K_b | \kappa_4 + K_\beta) \qquad (4.3.5)$$

Now for one-dimension the functions proposed by Young and March
obey equations (4.3.1) and (4.3.4) if we force periodicity in k_1
and k_2 (although this is not essential to the argument, only
affecting the precise nature of the labelling of the $v(k_1 \; k_2)$

with K_m and K_n), for, putting $y(x) = p(x) + x$, p a periodic function, the above author's functions (equation (5.2) of their paper) may be rewritten

$$\phi_{k_1 k_2}(x_1 x_2) = \frac{1}{\sqrt{2}} \left[\psi_{k_1 k_2}(x_1 x_2) - \psi_{k_2 k_1}(x_2 x_1) \right]$$

with

$$\psi_{k_1 k_2}(x_1 x_2) = \left\{ \frac{\partial}{\partial x}(x_1 - x_2) \right\}^{\frac{1}{2}} e^{i(k_1 - k_2)P(x_1 - x_2)} e^{ik_1 x_1} e^{ik_2 x_2}$$

$$(4.3.6)$$

It will be seen that this is of such a form that

$$v(k_1 + K_a | k_2 + K_b) = 0, \quad K_a + K_b \neq 0.$$

Hence from equation (4.3.5)

$$C(k_1 k_2 | k_3 k_4 | ..) v(k_1 + K_a | k_2 - K_a) v(k_3 + K_\alpha | k_4 - K_\alpha) = 0$$

unless $\quad K_a = K_\alpha.$

Now if we are to obtain a second order density matrix of form (4.1.1), then we must be able to find for a given k_1 $k_2 (k_1 \neq k_2)$ a value of K_α and values of k_3 k_4 ... k_{2N} such that

$$C(k_1 k_2 | k_3 k_4 | ..) v(k_3 + K_\alpha | k_4 - K_\alpha) \neq 0.$$

But then

$$v(k_1 + K_a | k_2 - K_a) = 0 \qquad \text{unless } K_a = K_\alpha.$$

This shows $\psi_{k_1 k_2}$ to be simply a product of two plane waves, which result must hold for all k_1, k_2. We have thus shown that method (B) of the Young-March scheme in one dimension is only variationally valid when it reduces to the Hartree-Fock result

(the wave function then being simply a determinant of plane waves).

It must be remarked that Young and March were unable to prove the satisfaction of the Pauli conditions on the first order density matrix in their method (B). However, it is known that satisfaction of the Pauli conditions does not ensure a variationally valid scheme, and it would appear that we must ensure the existence of a wave function directly. Nevertheless, the above example shows that it may not be necessary to explicitly build up the wave function to examine the validity of particular trial forms of the two-body orbitals of equation (4.1.1).

5. Localised orbital method (with M. Darby)

We turn now to discuss an explicit method of setting up a trial second-order density matrix. No really accurate form for the whole range of electron densities has, as yet, been found, but the method outlined here should be valid for densities which are not too high.

5.1 First and second-order matrices

The energy of the uniform system of any density may be written as

$$\epsilon = -\frac{1}{2\lambda^2}\int\left[\nabla_{\underline{r}}^2\,\gamma(\underline{r}'\underline{r})\right]_{\underline{r}'=\underline{r}}d\underline{r} + \frac{1}{2\lambda}\int d\underline{r}'\int d\underline{r}\,\frac{[2P(\underline{r}'\underline{r})-1]}{|\underline{r}'-\underline{r}|}$$

(5.1.1)

where the energy is in atomic units, and

$$\lambda = \left(\frac{4\pi}{3}\right)^{\frac{1}{3}} r_s,$$

r_s being the mean interparticle spacing, and $\gamma(\underline{r}'\underline{r})$ and the pair function $P(\underline{r}'\underline{r})$ are for a gas of uniform density. We take for the paramagnetic gas

$$2\Gamma(\underline{r}_1\underline{r}_2'\;\underline{r}_1\underline{r}_2) = \sum_{\underline{R}_n}{}' a^*(\underline{r}_2'-\underline{r}_1-\underline{R}_n)\,a(\underline{r}_2-\underline{r}_1-\underline{R}_n)$$

(5.1.2)

The $\underline{R}_n$ are vectors of a body-centred lattice, and the prime on the summation sign indicates that $\underline{R}_n = 0$ is excluded. $a(\underline{r})$ is a Wannier function for a simple cubic lattice (the b.c. lattice

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being made up of two of the simple cubic lattices) which has nodes at all the lattice points of the simple cubic lattice.

We form the first order density matrix from

$$\gamma(\underline{r}_2' \underline{r}_2) = \frac{2}{N-1} \int \Gamma(\underline{r}_1 \ \underline{r}_2' \ \underline{r}_1 \ \underline{r}_2) d\underline{r}_1. \qquad (5.1.3)$$

We write

$$a(\underline{r}) = \frac{1}{\Omega_B} \int v(\underline{k}) \ e^{i\underline{k}\cdot\underline{r}} \ d\underline{k}. \qquad (5.1.4)$$

Ω_B is the Brillouin zone for the simple cubic lattice (the vectors of which we shall denote by $\underline{S}_n$). Inserting (5.1.4) in (5.1.3) and letting $N \to \infty$ we obtain

$$\gamma(\underline{r}_1 \ \underline{r}_2) = \frac{8\pi^3}{\Omega_B^2} \int |v(\underline{k})|^2 \ e^{i\underline{k}\cdot(\underline{r}_1 - \underline{r}_2)} \ d\underline{k}.$$

The kinetic energy is therefore given by

$$- \frac{1}{2\lambda^2} \int \nabla^2 \gamma(\underline{r}' \underline{r})_{\underline{r}' = \underline{r}} \ d\underline{r} = - \frac{1}{2\lambda^2} \frac{8\pi^3}{\Omega_B^2} \int d\underline{r} \int |v(k)|^2 \ k^2 \ dk,$$

so that kinetic energy per particle is

$$T = - \frac{1}{2\lambda^2} \frac{8\pi^3}{\Omega_B^2} \int |v(\underline{k})|^2 \ k^2 \ dk$$

which may be rewritten

$$T = - \frac{1}{2\lambda^2} \int a^{\ast}(\underline{r}) \ \nabla^2 \ a(\underline{r}) \ d\underline{r} \qquad (5.1.5)$$

It may be noted that we antomatically satisfy the Pauli condition that the occupation numbers are less than one,

$$0 < a(\underline{k}) < 1,$$

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for we can form a Bloch function

$$\psi_{\underline{k}}(\underline{r}) = \sum_{\underline{R}_n} a(\underline{r}-\underline{R}_n)e^{i\underline{k}\cdot\underline{R}_n} = \sum_{\underline{K}_n} v(\underline{k}+\underline{K}_n)e^{i(\underline{k}+\underline{K}_n)\cdot\underline{r}}$$

and this normalises to unity over the unit cell:

$$1 = \int_\Omega |\psi_{\underline{k}}(\underline{r})|^2 \; d\underline{r} = \Omega \sum_{\underline{K}_n} |v(\underline{k}+\underline{K}_n)|^2 .$$

Hence

$$v(\underline{k}) < \frac{1}{\Omega} \quad \text{everywhere.}$$

For the potential energy, since $P(\underline{r}'\underline{r}) = P)\underline{r}'-\underline{r})$, we obtain per particle

$$V = \frac{1}{2\lambda} \int \frac{[2P(\underline{r})-1]}{r} \; d\underline{r}$$

Now

$$2P(\underline{r}) = \sum_{\underline{R}_n}{}' |a^{\underline{x}}(\underline{r}-\underline{R}_n)|^2$$

We therefore have

$$V = \frac{1}{2\lambda} \left\{ \sum_{\underline{R}_n}{}' \int \frac{|a(\underline{r})|^2}{|\underline{r}-\underline{R}_n|} \; d\underline{r} \; - \int \frac{d\underline{r}}{r} \right\} \qquad (5.1.6)$$

Hence the potential energy is just that of the orbital $a(\underline{r})$ centred at the origin in the fields of point charges, one at every other lattice site (the term $\int \frac{d\underline{r}}{r}$ will be ignored below,

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cancelled by the self energy of the uniform background charge).

If we form the periodic potential

$$V(\underline{r}) = \sum_{\underline{R}_n} \frac{1}{|\underline{R}_n - \underline{r}|} \tag{5.1.7}$$

we may write the total energy per particle as

$$\frac{\xi}{N} = -\frac{1}{2\lambda^2} \int a^{\pm} \nabla^2 a \, d\underline{r} + \frac{1}{2\lambda} \left\{ \int V(\underline{r}) \, a(\underline{r})^2 \, d\underline{r} - \int \frac{|a(\underline{r})|^2}{r} \, d\underline{r} \right. \tag{5.1.8}$$

where we have taken the mean value of $V(\underline{r})$ as zero. This is of no consequence when we seek Euler equations with particular trial forms of $a(\underline{r})$ such as the one we now examine.

5.2 The Macke Transformed Wannier Functions

In order to generalize the scheme outlined above, we replace the functions $a(\underline{r})$ by Macke-transformed simple cubic Wannier functions, given by:-

$$(X_1 Y_1 Z_1)^{\frac{1}{2}} \, \alpha_x(X) \, \alpha_y(Y) \, \alpha_z(Z) = J^{\frac{1}{2}} \, \alpha(\underline{R}) \tag{5.2.1}$$

Here $X = X(x)$, $Y = Y(y)$, $Z = Z(z)$, and we restrict these transformations so that $X_1(x+S_x) = X_1(x)$; $X_1(x) = X_1(-x)$. Further $X_1 = dX/dx$; $X_2 = d^2X/dx^2$, etc., and the simple cubic Wannier function α_x is defined by

$$\alpha_x(X) = \frac{1}{\Omega_B \Omega^{\frac{1}{2}}} \int_{\Omega_B} e^{ikX} \, dk$$

Ω and Ω_B are respectively the volumes of the unit cell for the

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simple cubic lattice, which has vectors $\underset{\sim}{S}_n$, and the Brillouin zone for the same lattice, and are thus related through:-

$$\Omega\Omega_B = 8\pi^3.$$

It is convenient to quote here certain summation rules for the simple cubic Wannier functions. Defining the length b by $\Omega_B = 8b^3$, we have

$$\sum_{\underset{\sim}{S}_n} \alpha^*(\underset{\sim}{r}-\underset{\sim}{S}_n) \, \alpha(\underset{\sim}{r}-\underset{\sim}{S}_n) = {}^1/\Omega.$$

$$\sum_{\underset{\sim}{S}_n} \alpha^*(\underset{\sim}{r}-\underset{\sim}{S}_n) \frac{d}{dx} \alpha(\underset{\sim}{r}-\underset{\sim}{S}_n) = \sum_{\underset{\sim}{S}_n} \alpha^*(\underset{\sim}{r}-\underset{\sim}{S}_n) \frac{d^3}{dx^3} \alpha(\underset{\sim}{r}-\underset{\sim}{S}_n) = 0$$

$$\sum_{\underset{\sim}{S}_n} \alpha^*(\underset{\sim}{r}-\underset{\sim}{S}_n) \frac{d^2}{dx^2} \alpha(\underset{\sim}{r}-\underset{\sim}{S}_n) = - \sum_{\underset{\sim}{S}_n} \frac{d}{dx} \alpha^*(\underset{\sim}{r}-\underset{\sim}{S}_n) \frac{d}{dx} \alpha(\underset{\sim}{r}-\underset{\sim}{S}_n)$$

$$= - \frac{b^2}{3\Omega}. \qquad (5.2.2)$$

These will be needed in obtaining Euler equations, but before we do this, we must see what energy expression (5.1.8) becomes when we replace $a(\underset{\sim}{r})$ by the transformed function (5.2.1).

The kinetic energy term consists of an integral over all space, the x-component of the integrand of which is just,

$$Y_1 Z_1 Z_1{}^{\frac{1}{2}} \alpha_y{}^2 \alpha_z{}^2 \left\{ \alpha_x{}^2 \left[\frac{X_3}{2X_1{}^{\frac{1}{2}}} - \frac{X_2{}^2}{4X_1{}^{\frac{3}{2}}} \right] + \alpha'_x \alpha_x \left[2X_2 X_1{}^{\frac{1}{2}} \right] + \alpha''_x \alpha_x X_1{}^{\frac{3}{2}} \right\},$$

where $\alpha'_x = d\alpha_x/dx$, etc. Similar terms hold for the y and z

components. Now since $X(x)$ is periodic in the lattice, we may replace the integral over all space by a sum of integrals over one zone, and then employing the summation rules (5.2.2) we obtain for the kinetic energy per particle:-

$$\frac{1}{2\lambda^2} \int_\Omega \left\{ \frac{X_3}{4} - \frac{X_2^2}{8X_1} - \frac{b^2}{3\Omega} X_1^3 \right\} Y_1 Z_1 \, d\underset{\sim}{r} + \text{similar terms for y and z components.}$$

$$(5.2.3)$$

In order to obtain an Euler equation we require the energy to be in the form of an integral over all space, and thus we introduce the first of the summation rules (5.2.2) into (5.2.3), obtaining:-

$$\frac{\Omega}{2\lambda^2} \int_{\text{All space}} \left\{ \frac{X_3}{4} - \frac{X_2^2}{8X_1} - \frac{b^2}{3\Omega} X_1^3 \right\} Y_1 Z_1 \, \alpha^\ast(\underset{\sim}{r})\alpha(\underset{\sim}{r})d\underset{\sim}{r} + \text{similar terms for y and z components.}$$

Replacing $a(\underset{\sim}{r})$ by the transformed functions (5.2.1) in the Potential energy part of (5.1.8), we obtain

$$\frac{1}{2\lambda} \int_{\text{All space}} d\underset{\sim}{r} \ [V(\underset{\sim}{r}) - \frac{1}{r}] \ Y_1 Z_1 X_1 \ \alpha^\ast(\underset{\sim}{R}) \ \alpha(\underset{\sim}{R})$$

$$= \frac{1}{\lambda\Omega2} \int_\Omega V'(\underset{\sim}{r}) X_1 Y_1 Z_1 \, d\underset{\sim}{r} - \frac{1}{2\lambda} \int_{\text{All space}} \frac{1}{r} X_1 Y_1 Z_1 \ \alpha^\ast(\underset{\sim}{R})\alpha(\underset{\sim}{R})d\underset{\sim}{r}$$

Here $V'(\underset{\sim}{r})$ is a localised potential. Again using the first summation rule of (5.2.2) on the first term we obtain finally for the potential energy per particle:-

$$\frac{1}{2\lambda} \int\limits_{\text{All space}} V(\underset{\sim}{r}) X_1 Y_1 Z_1 \ \alpha^{\ast}(\underset{\sim}{r}) \alpha(\underset{\sim}{r}) d\underset{\sim}{r} - \frac{1}{2\lambda} \int\limits_{\text{All space}} \frac{1}{r} X_1 Y_1 Z_1 \ \alpha^{\ast}(\underset{\sim}{R}) \alpha(\underset{\sim}{R}) d\underset{\sim}{r}$$

$$(5.2.5)$$

The total energy per particle, using Macke transformed simple cubic Wannier functions in this scheme, is thus given by the sum of (5.2.4) and (5.2.5). We proceed now to obtain the Euler equations for the transformation functions X,Y,Z. Functions satisfying these equations will give the lowest bound of the energy as given by (5.2.4) and (5.2.5).

5.3 The Euler Equations

If we write the energy of our system in the form

$$\epsilon = \int\limits_{\text{All space}} I(X,Y,Z,X_1,Y_1,Z_1,X_2,Y_2,Z_2) dx\,dy\,dz$$

then the functions X,Y,Z making ϵ a minimum satisfy the Euler equations for our scheme. The variations in X,Y,Z must be considered separately, and in particular, for the variations in X we have:-

$$\delta_x \epsilon = 0 = \int\limits_{-\infty}^{\infty} dx \int\limits_{-\infty}^{\infty} dy \int\limits_{-\infty}^{\infty} dz \ \delta_x \ I$$

Assuming I to be zero at the limits $x = \pm \infty$, we may write

$$\int\limits_{-\infty}^{\infty} dy \int\limits_{-\infty}^{\infty} dz \ \delta_x I = 0 \qquad (5.3.1)$$

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As $X \to X + \delta X$; $X_1 \to X_1 + \delta X_1$; $X_2 \to X_2 + \delta X_2$, thus:-

$$\delta_x I = \frac{\partial I}{\partial X} \delta X + \frac{\partial I}{\partial X_1} \delta X_1 + \frac{\partial I}{\partial X_2} \delta X_2$$

Further

$$\int \frac{\partial I}{\partial X_1} \delta X_1 \, d\underset{\sim}{r} = \int dy \, dz \, \frac{\partial I}{\partial X_1} [\delta X]_{-\infty}^{\infty} - \int \frac{\partial}{\partial x} \frac{\partial I}{\partial X_1} \delta X \, d\underset{\sim}{r}$$

By our previous assumptions the first term on the R.H.S. is zero .
Similarly

$$\int \frac{\partial I}{\partial X_2} \delta X_2 \, d\underset{\sim}{r} = \int \frac{\partial^2}{\partial x^2} \frac{\partial I}{\partial X_2} \delta X \, d\underset{\sim}{r}$$

Now since δX is arbitary, the integrand with respect to X must
vanish for all X, (but only X) so that (5.3.1) becomes

$$\int_{-\infty}^{\infty} dy \int_{-\infty}^{\infty} dz \left\{ \frac{\partial I}{\partial X} - \frac{\partial}{\partial x} \frac{\partial I}{\partial X_1} + \frac{\partial^2}{\partial x^2} \frac{\partial I}{\partial X_2} \right\} = 0 \qquad (5.3.2)$$

Similar expressions hold for variations with respect to Y and Z, but
here we will confine our attention to those with respect to X,
the Euler equation for Y and Z being obtained by changing the
variables in a cyclic way.

In evaluating (5.3.2) it is convenient to consider the
kinetic and potential energy terms separately. For the kinetic
energy part, I is the integrand of (5.2.4). Evaluating the
derivatives and combining terms we have for the kinetic energy
contribution to the Euler equation:-

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$$\frac{\Omega}{2\lambda^2} \int\limits_{-\infty}^{\infty} dy \int\limits_{-\infty}^{\infty} dz \; Y_1 Z_1 \left\{ \alpha^2(\underline{r}) \left[\frac{d}{dx} \left\{ -\frac{X_3}{4X_1} + \frac{X_2{}^2}{4X_1{}^2} - \frac{X_2{}^2}{8X_1{}^3} + \frac{b^2}{\Omega} X_1{}^2 \right\} \right] \right.$$

$$+ 2\alpha'(\underline{r})\alpha(\underline{r}) \left[-\frac{X_3}{4X_1} + \frac{X_2{}^2}{2X_1{}^2} - \frac{d}{dx} \left(\frac{X_2}{4X_1} \right) + \frac{X_2{}^2}{8X_1{}^3} - \frac{b^2}{\Omega} X_1{}^2 \right]$$

$$\left. + \frac{d}{dx} \left(2\alpha'(\underline{r})\alpha(\underline{r}) \right) \left[-\frac{X_2}{4X_1} \right] \right\}$$

The infinite integrals may now be written as sums of integrals over the sides of the simple cubic unit cell. Since we have only two integrations we obtain a sum $\sum S_y, S_z$, where S_y, S_z are the y and z components of $\underline{S}_n$ respectively. In order to use the summation rules (5.2.2) it is convenient to introduce a further summation, over S_x, but it should be noted that this now has to be carried throughout the working. Using the summation rules we obtain

$$\frac{1}{\lambda^2} \left[\frac{d}{dx} \left\{ -\frac{X_3}{4X_1} + \frac{X_2{}^2}{8X_1{}^2} + \frac{b^2}{\Omega} \right\} \right] \int\limits_{-a}^{a} Y_1 dy \int\limits_{-a}^{a} Z_1 dz \qquad (5.3.3)$$

where a is defined by $\Omega = 8a^3$.

Using expression (5.2.5) we find that the potential energy term contributes

$$\frac{1}{2\lambda} \int\limits_{-\infty}^{\infty} dy \int\limits_{-\infty}^{\infty} dz \; Y_1 Z_1 \left\{ \alpha^2(\underline{R}) \frac{d}{dx} \left(\frac{1}{r} \right) - \alpha^2(\underline{r}) \frac{d}{dx} V(\underline{r}) \right.$$

$$\left. - V(\underline{r}) 2\alpha(\underline{r}) \alpha'(\underline{r}) \right\}$$

For the terms involving $V(\underline{r})$, the infinite integrals can again

by replaced by sums of integrals over the sides of the unit
cell, and to allow use of (5.2.2), and for consistency with
(5.3.3) we sum over S_x. Thus we obtain:-

$$- \frac{1}{2\Omega\lambda} \int_{-a}^{a} dy \int_{-a}^{a} dz\ Y_1 Z_1 V(\underline{r}) + \frac{1}{2\lambda} \sum_{S_x} \int_{-\infty}^{\infty} dy \int_{-\infty}^{\infty} dz\ Y_1 Z_1 \alpha^2 (R-S_x) \frac{d}{dx} (\frac{1}{r-S_x})$$

$$(5.3.4)$$

The Euler equation for X is now obtained by putting the sum of
(5.3.3) and (5.3.4) equal to zero. Before doing this we note
that if we choose the density of our system, γ

$$\gamma = \frac{N}{V} = \frac{h^3 k_f^3}{3\pi^2} = \frac{2}{\Omega}$$

equal to unity, then we find:-

$$\Omega = 2; \quad a = 2^{-\frac{2}{3}}; \quad b = \pi 2^{-\frac{1}{3}}$$

Then we have:-

$$\int_{-a}^{a} Y_1 dz \int_{-a}^{a} Z_1\ dx = 4a^2 = 2^{\frac{2}{3}}$$

Finally, since $X_1 Y_1 Z_1$ are assumed to have the same functional
form, F say, we may generalize the above terms for X_1 and obtain
for our transformation function F the Euler equation:-

$$\frac{2^{\frac{2}{3}}}{8\lambda^2} \frac{d}{dx} \left[-\frac{F_3(x)}{F_1(x)} + \frac{F_2{}^2(x)}{2F_1{}^2(x)} + 2^{\frac{1}{3}}\pi F_1{}^2(x) \right] - \frac{1}{4\lambda} \int_{-a}^{a} dy \int_{-a}^{a} dz\ F_1(y)F_1(z)V(\underline{r})$$

$$+ \frac{1}{2\lambda} \frac{d}{dx} \sum_{S_x} \int_{-\infty}^{\infty} dy \int_{-\infty}^{\infty} dz\ F_1(y)F_1(z) \frac{\alpha^2\{F(y)\}\alpha^2\{F(z)\}}{[(x-S_x)^2+y^2+z^2]^{\frac{1}{2}}} \alpha^2\{F(x) - S_x\} = 0$$

$$(5.3.5)$$

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This equation gives the best transformation functions F.
It may be observed that in the limits of high and low densities;
$F(x) = x$ gives the plane wave result in the limit $\lambda \to 0$, and
$F_1(x) = \sum_1 \delta(x - R_x^i)$ is a solution in the limit $\lambda \to \infty$.
Work is proceeding on the detailed properties
of the solution of these Euler equations.

6. Non-uniform electron gas (with S. Sampanthar)

So far, we have considered the influence of correlation effects in a uniform electron gas. Unfortunately, this Sommerfeld model neglects certain features which are of central importance in the theory of metals, and in particular averages out the periodic potential due to the ions to a constant value.

Very recently, Bellemans and De Leener (1961) have reported a many-body approach to the non-uniform gas problem. Their results, which were simply quoted without proof, have apparently been obtained by expanding the grand partition function of the system in powers of the coupling parameter between electrons and the positive (point) ions and between pairs of electrons. By summing infinite series of divergent terms, they were able to obtain finite results for the energy per particle. We show below that, by finding Dirac's density matrix in a self-consistent framework, we obtain a result which is closely connected to their final energy formula. Indeed, this may be obtained almost at once for our theory, if we add the Gellmann-Brueckner correlation energy for a high density uniform gas to the energy calculated from our approach.

6.1 Energy and Dirac density matrix of a non-uniform electron gas

We shall consider the problem of electrons moving in a periodic lattice of protons, in order to circumvent at present the difficulties of introducing Hartree fields associated with inner electrons, and for the conduction electrons we shall adopt essentially a Hartree description. We first write down the diagonal element $\rho(\vec{r})$ of Dirac's density matrix, to first order in the Hartree periodic potential $V(\vec{r})$, using the density matrix perturbation theory of March and Murray (1961). If k_f is the magnitude of the wave-vector at the Fermi surface, and if we use atomic units throughout, we have then

$$\rho(\vec{r}) = \frac{k_f^3}{3\pi^2} - \frac{2k_f^2}{\pi^2} \int d\vec{r}_1 \; \frac{V(\vec{r}_1)\; j_1(2k_f|\vec{r} - \vec{r}_1|)}{|\vec{r} - \vec{r}_1|^2} \; , \qquad (6.1.1)$$

where $j_1(\rho) = (\sin \rho - \rho \cos \rho)/\rho^2$. We see from (6.1.1) that the constant density $\rho_0 = k_f^3/3\pi^2$ is modulated by the periodic density correction, which we denote by ρ_1. We now introduce the Fourier components $V(\vec{\kappa}_n)$ of the Hartree potential $V(\vec{r})$ through

$$V(\vec{r}) = \sum_{\vec{\kappa}_n} V(\vec{\kappa}_n)\; e^{i(\vec{\kappa}_n \cdot \vec{r})} \qquad (6.1.2)$$

where the $\vec{\kappa}_n$ are reciprocal-lattice vectors, and we impose self-consistency through the Poisson equation,

$$\nabla^2 V(\vec{r}) = 4\pi \sum_{\vec{H}_n} \delta(\vec{r} - \vec{H}_n) - 4\pi\rho(\vec{r})$$

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$$= \frac{4\pi}{\Omega} \sum_{\vec{\kappa}_n} e^{i\vec{\kappa}_n \cdot \vec{r}} - 4\pi\rho(\vec{r}), \qquad (6.1.3)$$

where the $\vec{K}_n$ denote vectors in the direct lattice and Ω is the volume of the unit cell. Hence, substituting (6.1.1) and (6.1.2) in (6.1.3) and using the result that

$$J(k_f, \kappa_n) = \frac{2k_f^2}{\pi^2} \int d\vec{r} \, e^{i\kappa_n \cdot \vec{r}} \, \frac{j_1(2k_f r)}{r^2}$$

$$= \frac{2k_f}{\pi} + \left(\frac{2k_f^2}{\pi \kappa_n} - \frac{\kappa_n}{2\pi} \right) \ln \left| \frac{2k_f + \kappa_n}{2k_f - \kappa_n} \right| \qquad (6.1.4)$$

we find

$$V(\vec{\kappa}_n) = - \frac{4\pi/\Omega}{\kappa_n^2 + J(k_f, \kappa_n)} , \qquad \vec{\kappa}_n \neq 0, \qquad (6.1.5)$$

$$= 0, \qquad \vec{\kappa}_n = 0. \qquad (6.1.6)$$

This result, combined with (6.1.1) and (6.1.2), defines the self-consistent electron density in this approximation.

We next write down the potential energy U in the Hartree approximation. If V_N and V_e denote the potentials due to the nuclei and the electronic charge distribution respectively, then $V = V_N + V_e$ and it may readily be shown from the full Hamiltonian that the potential energy is given by

$$U = U_{NN} + \int d\vec{r} \, \rho \, V_N + \tfrac{1}{2} \int d\vec{r} \, \rho \, V_e, \qquad (6.1.7)$$

where U_{NN} is the Coulomb interaction energy of the unscreened

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protons; the second term is the electron-nuclear interaction
energy and the third the electron-electron potential energy.
Separating off the Madelung energy of the proton lattice in a
uniform background of electrons with density ρ_0, we may rewrite
(6.1.7) in the form

$$U = U_{Madelung} + \tfrac{1}{2} \int d\vec{r}\ \rho_1(\vec{r})\ V(\vec{r}) + \tfrac{1}{2} \int d\vec{r}\ \rho_1(\vec{r})\ V_N(\vec{r}), \quad (6.1.8)$$

where we have used the fact that $\int d\vec{r}\ \rho_1(\vec{r}) = 0$. To obtain the
total energy E we must add the kinetic energy contribution, which
in the density-matrix perturbation-theory has been given by
Corless and March (1961) as

$$T = T_{Fermi} + \frac{k_f^4}{\pi^3} \iint d\vec{r}_1\ d\vec{r}_2\ V(\vec{r}_1)\ V(\vec{r}_2)$$

$$\times \frac{j_1(2k_f\ \vec{r}_2 - \vec{r}_1)}{(2k_f\ \vec{r}_2 - \vec{r}_1)^2} + O(V^3), \quad (6.1.9)$$

where the first term is the usual Fermi energy for free electrons.
Rewriting (6.1.9) in terms of ρ_1 defined from (6.1.1), it is
immediately seen that the second term in (6.1.9) cancels the
second term in (6.1.8) when we form E = T + U. Thus we find

$$E = T_{Fermi} + U_{Madelung} + \tfrac{1}{2} \int d\vec{r}\ \rho_1(\vec{r})\ V_N(\vec{r}). \quad (6.1.10)$$

The last term can be evaluated by using the Fourier-series form
of ρ_1 and the fact that $V_N(\vec{r})$ is a sum of Coulomb potentials over

the lattice sites.   The contribution from this term to the energy per particle may then be readily obtained as

$$\sum \frac{V(\vec{\kappa}_n)}{2\kappa_n^2} \, J(k_f, \kappa_n). \qquad\qquad (6.1.11)$$

Adding the usual exchange and correlation energies to the Hartree energy derived above, we obtain the result of Bellemans and De Leener if the Fourier components $V(\vec{\kappa}_n)$ in (6.1.11) are replaced by the unscreened Coulomb values $4k_f^3/3\pi \, \kappa_n^2$.   Our result appears to have more direct physical significance in that screening is included from the outset.

6.2 Discussion of natural spin orbitals

A complete set of Bloch functions $\{\psi_{\underset{\sim}{k}}^{1}(\underset{\sim}{r})\}$ will be defined
by the expressions (for an infinite crystal)

$$\psi_{\underset{\sim}{k}}^{1}(\underset{\sim}{r}) = \sum_{\underset{\sim}{R}_n} a_i(\underset{\sim}{r}-\underset{\sim}{R}_n)e^{i\underset{\sim}{k}\cdot\underset{\sim}{R}_n} \tag{6.2.1}$$

$$\int_{\text{All space}} a_i^{*}(\underset{\sim}{r}-\underset{\sim}{R}_m)a_j(\underset{\sim}{r}-\underset{\sim}{R}_n)dr = \delta_{ij}\,\delta(\underset{\sim}{R}_m,\,\underset{\sim}{R}_n). \tag{6.2.2}$$

It follows that

$$\int_{\Omega} |\psi_{\underset{\sim}{k}}^{1}(\underset{\sim}{r})|^{2}\,d\underset{\sim}{r} = 1 \quad - \quad \text{the normalisation is independent of } \underset{\sim}{k}.$$

Now

$$\int_{\text{All space}} \psi_{\underset{\sim}{k}_1}^{1\,*}(\underset{\sim}{r})\,\psi_{\underset{\sim}{k}_2}^{j}(\underset{\sim}{r})d\underset{\sim}{r} = \sum_{\underset{\sim}{R}_m,\underset{\sim}{R}_n}\int a_i^{*}(\underset{\sim}{r}-\underset{\sim}{R}_m)\,a_j(\underset{\sim}{r}-\underset{\sim}{R}_n)e^{i\underset{\sim}{k}_2\underset{\sim}{R}_n}\,e^{-i\underset{\sim}{k}_1\cdot\underset{\sim}{R}_m}$$

$$= \delta_{ij}\sum_{\underset{\sim}{R}_n} e^{i(\underset{\sim}{k}_2-\underset{\sim}{k}_1)\cdot\underset{\sim}{R}_n}.$$

i.e.

$$\int_{\text{All space}} \psi_{\underset{\sim}{k}_1}^{*i}(\underset{\sim}{r})\psi_{\underset{\sim}{k}_2}^{j}(\underset{\sim}{r})d\underset{\sim}{r} = \Omega_B\,\delta_{ij}\sum_{\underset{\sim}{K}_m}\delta(\underset{\sim}{k}_1 - \underset{\sim}{k}_2 + \underset{\sim}{K}_m). \tag{6.2.3}$$

$\Gamma(\underset{\sim}{r},\underset{\sim}{r}')$, when defined for a finite crystal, will obey
periodic boundary conditions analogous to those imposed on the
one particle Bloch functions. These form a complete set so that

$\gamma(\underline{r}',\underline{r})$ may be expanded in terms of them over the domain of the crystal. We shall treat the infinite crystal case. We write

$$\gamma(\underline{r}',\underline{r}) = \sum_{ij} \int_{\Omega_B} d\underline{k}_1 \int_{\Omega_B} d\underline{k}_2 \ c_{ij}(\underline{k}_1,\underline{k}_2) \psi_{\underline{k}_1}^{*i}(r') \psi_{\underline{k}_2}^{j}(\underline{r}). \qquad (6.2.4)$$

To obtain the natural orbitals we must diagonalize $C_{ij}(\underline{k}_1,k_2)$. We shall show it to be already diagonal in $\underline{k}$.

Equation (6.2.4) only requires $C_{ij}(k_1,k_2)$ to be defined when $\underline{k}_1$ and $\underline{k}_2$ lie within the Brillouin zone. However, we shall for mathematical convenience take it doubly periodic in the sense

$$C_{ij}(\underline{k}_1+\underline{K}_m,\underline{k}_2+\underline{K}_n) = C_{ij}(\underline{k}_1,\underline{k}_2). \qquad (6.2.5)$$

Our results will follow from the imposition of the periodicity condition expressing the arbitrariness of origin in the crystal:

$$\gamma(\underline{r}'-\underline{R}_n,\underline{r}-\underline{R}_n) = \gamma(\underline{r}',\underline{r}). \qquad (6.2.6)$$

We define the mixed matrix

$$\gamma(\underline{\kappa},\underline{r}) = \int \gamma(\underline{r}',\underline{r}) \ e^{i\underline{\kappa}\cdot\underline{r}'} \ d\underline{r}'. \qquad (6.2.7)$$

All space

Thus

$$\gamma(\underline{\kappa},\underline{r}+\underline{R}_n) = \int \gamma(\underline{r}',\underline{r}+\underline{R}_n)e^{i\underline{\kappa}\cdot\underline{r}'} \ d\underline{r}' = \int \gamma(\underline{r}'+\underline{R}_n,\underline{r}+\underline{R}_n)e^{i\underline{\kappa}(\underline{r}'+\underline{R}_n)} \ d\underline{r}$$

i.e.

$$\gamma(\underline{\kappa},\underline{r})e^{i\underline{\kappa}\cdot\underline{R}_n} = \gamma(\underline{\kappa},\underline{r}+\underline{R}_n). \qquad (6.2.8)$$

Now since $\gamma(\kappa,r)$ is shown to be an eigenfunction, eigenvalue $e^{i\underset{\sim}{\kappa}\cdot\underset{\sim}{R}_n}$, of the translation operator $T_{\underset{\sim}{R}_n}$,

$$\gamma(\underset{\sim}{\kappa},\underset{\sim}{r}) = \sum_j C_j(\underset{\sim}{\kappa}) \psi_{\underset{\sim}{\kappa}}{}^j(\underset{\sim}{r}). \tag{6.2.9}$$

Let us now write,

$$\psi_{\underset{\sim}{k}_1}{}^{*i}(\underset{\sim}{r}') = \sum_{\underset{\sim}{K}_n} e^{-i(\underset{\sim}{k}_1+\underset{\sim}{K}_n)\cdot\underset{\sim}{r}'} V_i^{*}(\underset{\sim}{k}_1+\underset{\sim}{K}_n)$$

in equation (6.2.3). We see that

$$\gamma(\underset{\sim}{\kappa},\underset{\sim}{r}) = 8\pi^3 \sum_{ij} \int_{\Omega_B} d\underset{\sim}{k}\, C_{ij}(\underset{\sim}{\kappa},\underset{\sim}{\kappa})\, V_i^{*}(\underset{\sim}{\kappa})\, \psi_{\underset{\sim}{k}}{}^j(\underset{\sim}{r}),$$

or

$$\sum_j C_j(\underset{\sim}{\kappa})\, \psi_{\underset{\sim}{\kappa}}{}^j(\underset{\sim}{r}) = 8\pi^3 \sum_{ij} \int_{\Omega_B} d\underset{\sim}{k}\, C_{ij}(\underset{\sim}{\kappa},\underset{\sim}{\kappa}) V_i^{*}(\underset{\sim}{\kappa}) \psi_{\underset{\sim}{k}}{}^j(\underset{\sim}{r}).$$

Multiply through by $\psi_{\underset{\sim}{k}_0}{}^{\ell*}(\underset{\sim}{r})$ and integrate over all space. (6.2.3) shows that

$$\sum_j C_j(\underset{\sim}{\kappa})\delta_{j\ell}\sum_{\underset{\sim}{K}_n} \delta(\underset{\sim}{k}_0-\underset{\sim}{\kappa}+\underset{\sim}{K}_n) = 8\pi^3 \sum_{ij} \int_{\Omega_B} d\underset{\sim}{k}\, C_{ij}(\underset{\sim}{\kappa},\underset{\sim}{\kappa}) \sum_{\underset{\sim}{K}_n} \delta(k_0-\underset{\sim}{\kappa}+\underset{\sim}{K}_n)V_i^{*}(\underset{\sim}{\kappa})$$

or $C_j(\underset{\sim}{\kappa}) \sum_{\underset{\sim}{K}_n} \delta(\underset{\sim}{k}-\underset{\sim}{\kappa}+\underset{\sim}{K}_n) = 8\pi^3 \sum_i C_{ij}(\underset{\sim}{\kappa},\underset{\sim}{k}) V_i^{*}(\underset{\sim}{\kappa}).$

Intrating over the Brillouin zone with respect to $\underset{\sim}{k}$ and putting

$$C_{ij}(\underset{\sim}{\kappa}) = \int_{\Omega_B} C_{ij}(\underset{\sim}{\kappa},\underset{\sim}{k})d\underset{\sim}{k},$$

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$$C_j(\underset{\sim}{\kappa}) = 8\pi^3 \sum_1 C_{1j}(\underset{\sim}{\kappa}) \, V_1^{\textasteriskcentered}(\underset{\sim}{\kappa}). \qquad (6.2.10)$$

It should be noted that equation (6.2.5) implies the periodicity of $C_{1j}(\underset{\sim}{\kappa})$:

$$C_{1j}(\underset{\sim}{\kappa}+\underset{\sim}{K}_m) = C_{1j}(\underset{\sim}{\kappa}). \qquad (6.2.11)$$

Our expression for $\gamma(\underset{\sim}{\kappa},\underset{\sim}{r})$ may now be rewritten as

$$\gamma(\underset{\sim}{\kappa},\underset{\sim}{r}) = 8\pi^3 \sum_{1j} C_{1j}(\underset{\sim}{\kappa}) \, V_1^{\textasteriskcentered}(\underset{\sim}{\kappa}) \, \psi_{\underset{\sim}{\kappa}}^{\,j}(\underset{\sim}{r}).$$

Hence

$$\gamma(\underset{\sim}{r}',\underset{\sim}{r}) = \frac{1}{8\pi^3} \int \gamma(\underset{\sim}{\kappa},\underset{\sim}{r}) e^{-i\underset{\sim}{\kappa}\cdot\underset{\sim}{r}'} \, d\underset{\sim}{\kappa} = \sum_{1j} \int C_{1j}(\underset{\sim}{\kappa}) V_1^{\textasteriskcentered}(\underset{\sim}{\kappa}) \psi_{\underset{\sim}{\kappa}}^{\,j}(\underset{\sim}{r}) e^{-i\underset{\sim}{\kappa}\cdot\underset{\sim}{r}'} \, d\underset{\sim}{\kappa}$$

$$= \sum_{1j} \sum_{\underset{\sim}{K}_n} \int_{\Omega_B} C_{1j}(\underset{\sim}{\kappa}) V_1^{\textasteriskcentered}(\underset{\sim}{\kappa}+\underset{\sim}{K}_n) \psi_{\underset{\sim}{\kappa}}^{\,j}(\underset{\sim}{r}) e^{-i(\underset{\sim}{\kappa}+\underset{\sim}{K}_n)\cdot\underset{\sim}{r}'} \, d\underset{\sim}{\kappa}$$

i.e.

$$\gamma(\underset{\sim}{r}',\underset{\sim}{r}) = \sum_{1j} \int_{\Omega_B} C_{1j}(\underset{\sim}{k}) \psi_{\underset{\sim}{k}}^{\,1\textasteriskcentered}(\underset{\sim}{r}') \psi_{\underset{\sim}{k}}^{\,j}(\underset{\sim}{r}) \, d\underset{\sim}{k}. \qquad (6.2.12)$$

Let us consider the effect of applying a unitary transformation

$$\overline{C}_{k\ell}(\underset{\sim}{k}) = \sum_{1j} a_{k1}^{+}(\underset{\sim}{k}) C_{1j}(\underset{\sim}{k}) a_{j\ell}(\underset{\sim}{k}) = \sum_{1j} a_{1k}^{\textasteriskcentered}(\underset{\sim}{k}) C_{1j}(\underset{\sim}{k}) a_{j\ell}(k)$$

where

$$\sum_1 a_{k1}^{+}(\underset{\sim}{k}) a_{1\ell}(\underset{\sim}{k}) = \sum_1 a_{1k}^{\textasteriskcentered}(\underset{\sim}{k}) \, a_{1\ell}(\underset{\sim}{k}) = \delta_{k\ell}, \text{ independent of } \underset{\sim}{k}$$

and also define

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$$\phi_{\underset{\sim}{k}}^{\ell}(\underset{\sim}{r}) = \sum_n a_{n\ell}^{\text{x}}(\underset{\sim}{k})\psi_{\underset{\sim}{k}}^{n}(\underset{\sim}{r}); \quad \phi_{\underset{\sim}{k}}^{k\text{x}}(\underset{\sim}{r}) = \sum_m a_{mk}(\underset{\sim}{k})\psi_{\underset{\sim}{k}}^{m\text{x}}(\underset{\sim}{r}).$$

Then

$$\sum_{K\ell} \int_{\Omega_B} \overline{C}_{k\ell}(\underset{\sim}{k})\phi_{\underset{\sim}{k}}^{k\text{x}}(\underset{\sim}{r}')\phi_{\underset{\sim}{k}}^{\ell}(\underset{\sim}{r})d\underset{\sim}{r}$$

$$= \sum_{\substack{K\ell \\ ij \\ mn}} \int_{\Omega_B} a_{1k}^{\text{x}}(\underset{\sim}{k})C_{1j}(\underset{\sim}{k})a_{j\ell}(\underset{\sim}{k})a_{mk}(\underset{\sim}{k})a_{n\ell}^{\text{x}}(\underset{\sim}{k})\psi_{\underset{\sim}{k}}^{m\text{x}}(\underset{\sim}{r}')\psi_{\underset{\sim}{k}}^{n}(\underset{\sim}{r})d\underset{\sim}{k}$$

$$= \sum_{\substack{ijk\ell \\ mn}} \int_{\Omega_B} C_{1j}(\underset{\sim}{k})\delta_{jn}\delta_{1m} \psi_{\underset{\sim}{k}}^{m\text{x}}(\underset{\sim}{r}')\psi_{\underset{\sim}{k}}^{n}(\underset{\sim}{r})d\underset{\sim}{k}$$

$$= \sum_{ij} \int_{\Omega_B} C_{1j}(\underset{\sim}{k})\psi_{\underset{\sim}{k}}^{1\text{x}}(\underset{\sim}{r}')\psi_{\underset{\sim}{k}}^{j}(\underset{\sim}{r})d\underset{\sim}{k}.$$

We now prove that the set $\{\phi_{\underset{\sim}{k}}^{\ell}(\underset{\sim}{r})\}$ consists of Bloch functions by forming

$$\alpha_{\ell}(\underset{\sim}{r}) = \frac{1}{\Omega_B} \int_{\Omega_B} \phi_{\underset{\sim}{k}}^{\ell}(\underset{\sim}{r})d\underset{\sim}{k}$$

and demonstrating that

$$\int_{\text{All space}} \alpha_{\ell}^{\text{x}}(\underset{\sim}{r}-\underset{\sim}{R}_m)\alpha_p(\underset{\sim}{r}-\underset{\sim}{R}_n)d\underset{\sim}{r} = \delta_{\ell p} \delta(\underset{\sim}{R}_m,\underset{\sim}{R}_n)$$

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We have

$$\Omega_B \, \alpha_\ell(\underset{\sim}{r}) = \sum_n \int_{\Omega_B} a_{n\ell}{}^{\ast}(\underset{\sim}{k}) \, \psi_{\underset{\sim}{k}}{}^n(\underset{\sim}{r}) d\underset{\sim}{k} = \sum_n \sum_{\underset{\sim}{R}_\nu} a_n(\underset{\sim}{r}-\underset{\sim}{R}_\nu) \int_{\Omega_B} a_{n\ell}{}^{\ast}(\underset{\sim}{k}) e^{i\underset{\sim}{k}\cdot\underset{\sim}{R}_\nu} d\underset{\sim}{k}$$

Hence

$$\Omega_B{}^2 \int \alpha_\ell{}^{\ast}(\underset{\sim}{r}-\underset{\sim}{R}_m)\alpha_p(\underset{\sim}{r}-\underset{\sim}{R}_n)d\underset{\sim}{r} = \sum_{mn} \sum_{\underset{\sim}{R}_m,\underset{\sim}{R}_\nu} \int_{\Omega_B} d\underset{\sim}{k}_1 \int_{\Omega_B} d\underset{\sim}{k}_2$$

$$\times \, a_{m\ell}(\underset{\sim}{k}_1) e^{-i\underset{\sim}{k}_1\cdot\underset{\sim}{R}_m} a_{np}{}^{\ast}(\underset{\sim}{k}_2) e^{i\underset{\sim}{k}_2\cdot\underset{\sim}{R}_\nu} \int a_m{}^{\ast}(\underset{\sim}{r}-\underset{\sim}{R}_n-\underset{\sim}{R}_m) a_n(\underset{\sim}{r}-\underset{\sim}{R}_\nu-\underset{\sim}{R}_n)d\underset{\sim}{r}$$

$$= \sum_m \sum_{\underset{\sim}{R}_\nu} \int_{\Omega_B} d\underset{\sim}{k}_1 \int_{\Omega_B} d\underset{\sim}{k}_2 \, a_{m\ell}(\underset{\sim}{k}_1)a_{mp}{}^{\ast}(\underset{\sim}{k}_2) e^{i(\underset{\sim}{k}_2-\underset{\sim}{k}_1)\cdot\underset{\sim}{R}_\nu} e^{i\underset{\sim}{k}_1\cdot(\underset{\sim}{R}_n-\underset{\sim}{R}_m)}.$$

Or

$$\int \alpha_\ell{}^{\ast}(\underset{\sim}{r}-\underset{\sim}{R}_m)\alpha_\ell(\underset{\sim}{r}-\underset{\sim}{R}_n)d\underset{\sim}{r} = \frac{1}{\Omega_B} \int_{\Omega_B} d\underset{\sim}{k}_1 \, e^{i\underset{\sim}{k}_1\cdot(\underset{\sim}{R}_n-\underset{\sim}{R}_m)} \sum_m a_{m\ell}(\underset{\sim}{k}_1)a_{mp}{}^{\ast}(\underset{\sim}{k}_1)$$

$$= \frac{1}{\Omega_B} \int_{\Omega_B} d\underset{\sim}{k}_1 \, e^{i\underset{\sim}{k}_1\cdot(\underset{\sim}{R}_n-\underset{\sim}{R}_m)} \delta_{\ell p}.$$

The assertion is proved.

Now we note that because of the essential equivalence of
$\underset{\sim}{k}$ and $\underset{\sim}{k} + \underset{\sim}{K}_m$, $a{}^{\ast}{}_{\ell m}(\underset{\sim}{k})$ can be taken as periodic in $\underset{\sim}{k}$.

We see that $\{\phi_{\underset{\sim}{k}}{}^1(\underset{\sim}{r})\}$ is a set of Bloch functions for all
unitary transformations, including that making $C_{ij}(\underset{\sim}{k})$ diagonal.

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Thus

$$\gamma(\underline{r}',\underline{r}) = \sum_i \int_{\Omega_B} C_i(\underline{k}) \psi_{\underline{k}}^{i*}(\underline{r}') \psi_{\underline{k}}^{i}(\underline{r}) d\underline{r};$$

and the natural orbitals $\{\psi_{\underline{k}}^{i}(\underline{r})\}$ are Bloch functions.

To summarize, we can write

$$\gamma(\underline{r}',\underline{r}) = \sum_{ij} \int_{\Omega_B} d\underline{k}_1 \int_{\Omega_B} d\underline{k}_2 \, C_{ij}(\underline{k}_1,\underline{k}_2) \psi_{\underline{k}_1}^{i*}(\underline{r}') \psi_{\underline{k}_2}^{j}(\underline{r})$$

where $\{\psi_{\underline{k}}^{i}\}$ is a complete set of Bloch functions.

$C_{ij}(\underline{k}_1,\underline{k}_2)$ is shown to be diagonal with respect to $\underline{k}_1$ and $\underline{k}_2$ by consideration of the mixed matrix $\gamma(\kappa,r)$ which is such that

$$\gamma(\underline{k},\underline{r}+\underline{R}_n) = e^{i\underline{k}\cdot\underline{R}_n} \, \gamma(\underline{k},\underline{r}).$$

We show that if we apply unitary transformations $(a_{k\ell}(\underline{k})$ to the $(C_{ij}(\underline{k}))$ we obtain the set $\{\phi_{\underline{k}}^{i} = \sum_n a_{in}^{*}(\underline{k})\psi_{\underline{k}}^{n}\}$ which are shown to be Bloch functions.

The occupation numbers of the natural orbitals we obtained by applying unitary transformations diagonalising the $(C_{ij}(\underline{k}))$. The natural orbitals, obtainable by the same unitary transformation must therefore be Bloch functions.

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